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THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT AGATE

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(From the Raman Research Institute, Bangalore)

Received September 9, 1953

1. Introduction

It is well known that agate exhibits a banded structure. One explanation of the banding which has been put forward is that the agate is the result of the deposition of silica in an intermittent manner from liquids containing the material in solution. The assumed manner of formation is, however, clearly hypothetical and it leaves the question of the physical nature of the banding resulting therefrom unanswered. A different explanation that has been suggested and received with some favour is the so-called silica-gel theory. This regards the banded structure of agate as analogous in its nature to the periodic precipitates formed in gelatinous substances in certain circumstances. We may remark, however, that the characteristic structure of agate is observed even in the absence of any material other than silica in its composition. Further, it is to be noted that the microscope shows agate to be a coarsely crystalline material and not a colloid. The explanation of its banded structure as a Liesegang phenomenon in a colloidal gel appears in the circumstances to be rather far-fetched.

The question of the nature of the banded structure of agate presents itself in a particularly interesting form when we consider the case of the specimens exhibiting iridescence. It has long been known that the stratifications in agate may be so close and so regularly spaced as to enable a polished plate of the material to function as a diffraction grating when traversed by a beam of light. It is natural to suppose that a structure exhibiting such a high degree of regularity with strata following each other some 10,000 times in a centimetre is a consequence of some special feature in the aggregation of the crystallites of quartz of which agate is composed. The fact that we had at our disposal two examples of iridescent agate encouraged us to undertake a careful study of this question by optical and X-ray methods. The investigation has revealed several interesting facts, and besides elucidating the particular problem under consideration has also thrown fresh light on the structure and optical behaviour of non-iridescent agate and chalcedony.

2. SOME GENERAL OBSERVATIONS

Enlarged photographs of our two specimens are reproduced as Figs. 1 and 2 respectively in Plate XII. They exhibit a banded structure over the entire area of the plates except in a region adjacent to the irregular upper edge of specimen I where it is definitely absent, while in the case of specimen II, the banding gradually fades off and becomes inconspicuous as we approach the triangular tip of the plate at its lower end. In both cases the banding meets the surface in a series of curved lines running parallel to each other and exhibiting several sharply defined changes of direction. The iridescent area in each case is a strip about a centimetre in width running parallel to the banding and traversing the entire specimen from one side to the other. In Fig. 2 it appears as a series of conspicuous bands running across the middle of the specimen, while in Fig. 1 the strip appears perfectly dark in its first segment on the right, faintly banded in the middle segment, and quite bright in the third segment towards the left.

Figs. 3 and 4 in Plate XIII are photographs of a small section of the iridescent area on specimen II greatly enlarged. The two photographs were recorded respectively by transmitted and by diffracted light, and it will be recognised at once that they are complementary, the areas appearing bright in one picture, appearing dark in the other and *vice versa*. The photographs exhibit other features of interest to which we shall revert later. It may be remarked here that the complementarity which they exhibit is a feature which is noticeable with both of our specimens over the entire area exhibiting a banded structure, those regions which appear bright by diffracted light appearing dark by transmitted light, and *vice versa*. Viewed obliquely to the direction of the illuminating beam, both specimens in the non-iridescent areas show a bluish-white opalescence.

3. POLARISATION OF THE TRANSMITTED LIGHT

Our specimens I and II were respectively 3 and 2 millimetres thick. They are both noticeably transparent, but much more so in the case of the thinner specimen. In other words, a light-source such as an open window or the dome of an electric lamp could be seen through the agate with full definition in all its details, though overlaid by a field of diffuse radiation. As is to be expected, the areas exhibiting iridescence are much less transparent than the rest and they also impart a distinctly reddish tint to the light passing through them. *Per contra*, the non-banded areas near the upper edge of specimen I are distinctly more transparent than its banded areas, the yellowish-red tint of the transmitted light being however very conspicuous.

It is noteworthy that the intensity and colour of the light transmitted by our specimens are largely influenced by varying the inclination of the specimen with respect to the rays of light traversing it; the effect is very conspicuous when the specimen is so tilted that the plane of incidence remains normal to the planes of banding of the material. The maximum transmission is observed when the light rays are parallel to the planes of banding; the light transmitted diminishes rapidly in intensity and at the same time becomes a deeper red in colour when the light rays make increasingly larger angles with the planes of banding, until finally it is lost altogether in a notably strengthened background of diffuse light. A tilt of the specimen in the same plane as the banding layers produces an effect of the same nature which however is much less conspicuous.

A remarkable observation made by us is that *the light transmitted by our specimens is completely polarised when observed through the areas exhibiting a banded structure.* This is the case even when the banding is inconspicuous. Further, a tilt of the specimen with respect to the light rays which notably alters the intensity and colour of the transmitted light does not affect the totality of its polarisation. The direction of electric vibration in the transmitted light lies in a plane normal to the planes of banding in the specimen. When the area of observation is moved to another adjacent position in which the planes of banding have taken a sudden turn, the direction of vibration in the transmitted light takes a similar sudden turn. Likewise, as we move along the curved areas which represent the banding planes, the direction of vibration in the transmitted light swings round in the same fashion. It should finally be remarked that for those areas of our specimen I where no banding is visible and which allow a transmitted light of an yellowish-red colour, a marked though incomplete polarisation of the same is observable, the direction of vibration being approximately the same as in the neighbouring banded areas.

4. The Diffusion of Light Accompanying Transmission

When a small intense source of light is viewed through the banded non-iridescent areas of our specimens, we observe a phenomenon which is illustrated in Fig. 5 in Plate XIV. On either side of the light source as seen through the specimen we notice a fairly intense but a narrow bundle of diffused light stretching out in a direction parallel to the planes of banding. Further away, this spreads out both longitudinally and transversely into a diffuse brush of light of rapidly diminishing intensity.

As mentioned above, the image of the light source seen through the banded areas of our specimens is completely polarised. This effect is

demonstrated by Fig. 6 in Plate XIV which represents the light source as viewed through a non-iridescent area of the agate coupled with a double-image prism of quartz. Of the two images produced by this combination seen side by side in the figure, the one on the right hand has the electric vibration normal to the banding planes while for the one on the left, the vibration direction is parallel to these planes. It will be noticed that the image of the source appears only in the former and is totally absent in the latter. The vertical brush of light passing through the image is however seen in both images but is less intense in the latter, indicating that the brush is partially polarised in the same sense as the transmitted light. The farther away we move from the image of the light source in either direction, the less conspicuous becomes the difference in intensity between the two images. Owing to their overlap in the photograph, it is not possible to make a definite statement whether or not there is a reversal of the state of polarisation in the more distant parts of the brush.

5. THE DIFFRACTION SPECTRA

From Figs. 1 and 2 in Plate XII it is evident that the iridiscent strips in our specimens do not form a single continuous diffraction grating over their entire width but consist of several distinct gratings with intervening gaps. The photographs reproduced as Figs. 3 and 4 in Plate XIII show this very clearly; the strip contains six different gratings separated by intervals which are not iridescent and hence appear bright by transmitted light and dark by diffracted light. That the six gratings in the agate are dissimilar is apparent from the fact that the colours which they exhibit when it is viewed obliquely are not identical. That each individual grating is nearly perfect however is proved by the observation that when a source of monochromatic light is viewed through it, a series of well-defined and regularly spaced images formed by the diffracted light is seen; with a mercury arc lamp as source the two sets of images formed respectively by the green and yellow radiations are seen well separated. No images formed by the λ 4358 Å radiations are visible owing to the strong diffusion and lack of transparency of the agate in that region of the spectrum.

The spectra formed by the agate are not simply a series of images of the source. Actually, each spectrum including that of zero order is a diffusion pattern exhibiting the features already described and illustrated in Fig. 5 of Plate XIV with their specific polarisation characters. The geometric images of the source appearing in the spectra are completely polarised with their vibration directions perpendicular to the lines of the diffraction grating, while the vertical bundle of diffused light accompanying each image

exhibits a partial polarisation in the same sense. The diffuse brush appearing further out however exhibits a partial polarisation in the reverse sense, having its vibrations parallel to the lines of grating. These features are evident to inspection in Fig. 7 of Plate XIV which was recorded with a mercury arc as source and a double-image prism of quartz superposed on the agate to exhibit the two components of polarised light in each spectrum separately.

It may be remarked that the diffraction phenomena described above are notably influenced by tilting the grating with respect to the incident light rays in one plane or the other, as could have been anticipated from the observations of the same nature already reported for the non-iridescent areas. We may also make a brief reference to the diffraction phenomena which are observed when a light source is viewed through certain non-iridescent but conspicuously banded areas of the agate. They are of a much less striking character than those exhibited by the iridescent areas and will not here be described in detail.

6. Significance of the Results

The optical phenomena described above enable us to derive the following conclusions regarding the structure of the agate in the areas exhibiting the diffraction spectra:

I. The crystallites of quartz composing the agate arrange themselves in fibres along a direction normal to the planes of banding.

II. The principal axis of the quartz in the individual crystallites lies in the planes of banding.

III. Each fibre exhibits along its length a periodicity in the orientation of the principal axis of the quartz, such periodicity being the same for all the fibres.

The first proposition stated above follows directly from the nature of the diffusion patterns reproduced in Plate XIV.

The second proposition finds its justification in the observed fact that the light regularly transmitted by the banded regions is completely polarised with its vibrations normal to the planes of banding. Had the optic axis of the quartz in the crystallites been orientated *at random*, the birefringence of the quartz would have resulted in the agate not transmitting any part of the incident light but merely diffusing it. On the other hand, had the optic axes all been *normal to the planes of banding*, the light regularly transmitted would have exhibited both components of polarisation. If,

however, as indicated, the optic axes of all the crystallites lie *in the planes of banding*, the effective refractive index for a vibration normal to the planes of banding would be the same for all of them, while the index for a vibration in a transverse direction would vary from crystallite to crystallite. Hence the former component would be regularly transmitted, while the latter would be diffused and totally excluded from the transmitted light, in agreement with what is actually observed.

The third conclusion stated above follows inevitably if an aggregate of individual fibres is to function as a diffraction grating exhibiting the optical effects illustrated in Fig. 7 of Plate XIV. In the circumstances of the case, the only type of periodicity in optical properties which could be admitted is that the optic axis lies in different directions along the length of the fibre, repeating themselves at corresponding points in the diffraction grating.

7. THE X-RAY DIFFRACTION PATTERNS

As both of our specimens had sharply defined edges intersected by the banded structure, it was found easy to obtain X-ray diffraction patterns of the agate in selected regions. A narrow pencil of X-rays was allowed to graze the edge at the chosen region and the diffraction pattern was recorded with a flat-film camera. Figs. 8, 9 and 10 in Plate XV reproduce the patterns obtained in this manner using our specimen II and unfilterd X-radiation from a molybdenum target. Fig. 8 is the record for the region exhibiting strong iridescence, Fig. 9 for a region further down which was non-iridescent but exhibited visible banding and Fig. 10 at the triangular tip where no banding was visible at all. We have obtained very similar records with our other specimen, but these have not been reproduced. The striking differences observed in the X-ray patterns of different regions in the same specimen are a clear demonstration that the structure of agate is a consequence of the grouping of the crystallites in specific orientations along the planes of banding. The X-ray pattern of the iridescent area reproduced as Fig. 8 in Plate XV is readily identifiable as due to an aggregate of crystallites having one of the crystallographic *a*-axes as a common direction while the principal or *c*-axis assumes all possible orientations. This result is in full accord with the conclusions derived from the optical studies set forth earlier in the paper. The patterns reproduced in Figs. 9 and 10 show a less well-defined state of orientation of the crystallites. Indeed, in the latter, there is hardly any specificity of orientation indicated. This is not surprising since the banded structure of the agate is invisible near its extremity.

8. Some Further Observations

In the enlarged photographs of the iridescent agate (specimen II) reproduced in Plate XIII, it is possible to recognize a good deal of visible structure in the material. Of particular interest are the curious wavy patterns seen in some of the strips, both in transmitted and by diffracted light. Similar patterns are seen over the entire iridescent area of our specimen I by merely holding it up against a window and viewing it through a magnifier of moderate power. These patterns are best examined by placing the agate on the stage of a low-power binocular microscope and viewing it either by direct or by oblique illumination from below the stage. Very interesting effects are observed if between the agate and the objectives of the microscope a polaroid sheet is interposed and turned round in its own plane. *The wavy patterns are vividly seen when the polaroid has its vibration direction parallel to the planes of banding of the agate. But they disappear completely when the polaroid is set with its vibration direction perpendicular to the planes of banding.*

The significance of the results stated above becomes evident when one recognises the patterns as being of the same nature as those seen when two similar diffraction gratings which are not perfectly in register are held together and viewed against a source of light. In the present case, we are dealing with a single grating which extends through a considerable depth of the material. Hence, unless the structure is of extraordinary perfection, superposition patterns of the nature observed would necessarily arise. In the light of these remarks, the disappearance of the patterns when the light vector is normal to the planes of banding is highly significant. Such disappearance is to be expected if the grating has its origin in a periodicity of the orientation of the principal axis of the quartz along the length of each fibre. For, such periodicity would influence the retardation of light waves having their vector parallel to the planes of banding, but would leave unaffected the propagation of light having its vector normal to those planes.

9. Concluding Remarks

The ideas regarding the structure of iridescent agate set forth in Section 6 are thus independently supported by the X-ray patterns and by the optical evidence. It remains now to find a reason why the principal axis of quartz exhibits a periodicity in its setting along the length of the fibres in the iridescent regions. We wish here tentatively to put forward a suggestion regarding this matter. It is known that quartz exhibits a type of twinning in which the principal axis in the two components of the twin

are nearly at right angles to each other—more exactly make an angle of 84° 33′ with each other. It seems to us that the fibres of quartz in iridescent agate may be described as polysynthetic twins in which the alternate elements are related to each other presumably in the same manner as in the twins of the kind referred to.

10. SUMMARY

A detailed study has been made by optical and X-ray methods of two plates of banded agate which display iridescence over part of their area. The light transmitted by the banded areas is found to be completely polarised with the vector normal to the planes of banding. On the other hand, the wavy superposition patterns exhibited by the iridescent areas disappear for the same vibration direction. From these facts and the observed optical characters of the diffusion and diffraction phenomena it is deduced that the crystallites of quartz form fibres elongated in the direction of a crystallographic *a*-axis, while their principal or *c*-axes lie in the planes of banding but are orientated in a periodic manner in these planes so as to build up a structure which functions as a diffraction grating. The X-ray results support these findings. More generally also, they indicate that the banding of agate is a consequence of the presence in it of groups of crystallites of quartz having common specific orientations.

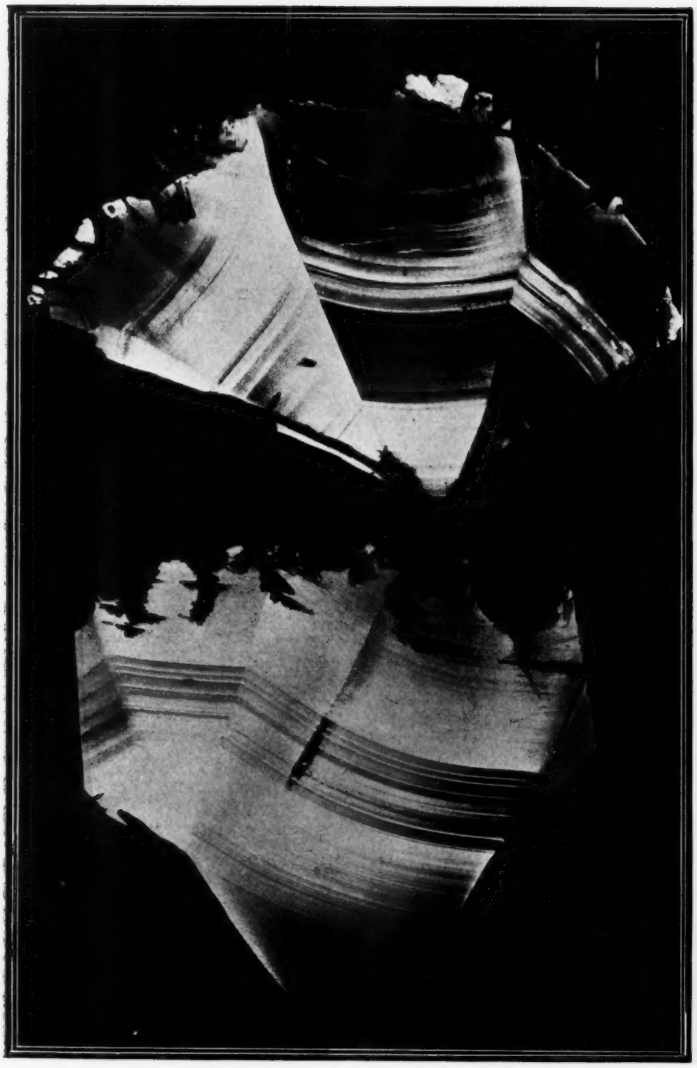

FIG. 1

FIG. 2

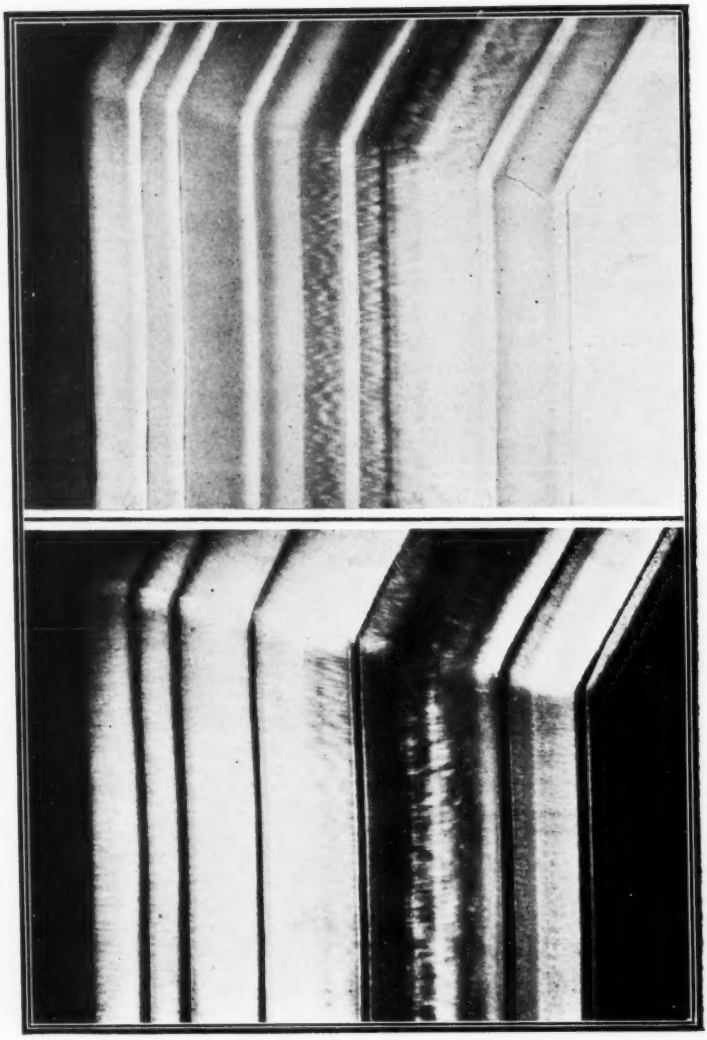

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

SYNTHETIC EXPERIMENTS IN THE BENZOPHYRONE SERIES

Part XXXVI. Nuclear Methylation of Nor-Eugenin and Chrysin, and Synthesis and Study of Related C-Methyl Compounds*

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(*From the Department of Chemistry, University of Delhi, Delhi*)

Received April 24, 1953

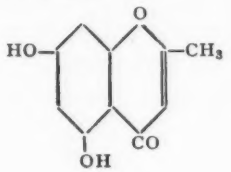
The phenomenon of nuclear methylation seems to be assuming increasing importance and to be also closely related to the more well-known phenomenon of nuclear oxidation in flavones and related compounds.[2] A detailed study of the course of nuclear methylation has therefore been considered to be useful. In laboratory experiments the first observation of nuclear methylation was made by Perkin and Horsfall[3] during their investigation of the constitution of genistein. When they used methyl iodide and methanolic potassium hydroxide, besides the normal dimethyl ether, they obtained as a minor product its C-methyl derivative. Similar results were reported by Perkin and Horsfall[4] in the methylation of the flavone luteolin and by Perkin[5] in the case of the flavonol quercetin. Since alkali fusion of these compounds gave C-methyl phloroglucinol monomethyl ether as a product, it was clear that the nuclear methyl group was present in the condensed benzene ring, but its location in the 6 or the 8 position was not established. However in the case of genistein, Baker and Robinson[6] suggested that the C-methyl group may be present in the 6-position based on analogy with the behaviour of simpler polyhydroxy carbonyl compounds. This suggestion has been supported by work done in this laboratory.[7]

But the above analogy may not be altogether adequate as the following consideration will show. Earlier work on β-substituted resorcinol derivatives, *e.g.*, aldehyde, carboxylic acid and ketone show that the γ-position is predominantly active not only in nuclear methylation[8] but also in other reactions such as allyl migration[9] and aldehyde synthesis.[10] It has been found that in flavones and chromones the predominantly reactive position is the 8-position and not the 6-position.[11] Hence there is need to make sure whether the methyl group enters the 6- or the 8-position adopting unambiguous methods. The present investigation has been undertaken

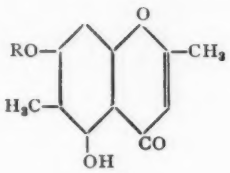
* See preliminary note on the above subject[1].

with a view to establish the constitution of these nuclear methylation products and is a continuation of our earlier work on the synthesis and study of C-methyl benzopyrone derivatives.[7, 12] Further a number of C-methyl benzopyrone compounds have recently been reported to occur in nature[13, 14, 15] and nuclear methylation may provide a convenient method of synthesis of some of these compounds.

The simplest compound of this type, *viz.*, 2-methyl-5: 7-dihydroxy chromone (nor-eugenin) (I)[12] has now been studied first. A number of C-methyl derivatives of this substance were reported earlier[12] and were readily available for direct comparison. Its nuclear methylation has now been carried out using excess of methyl iodide and methanolic sodium methoxide and the product is obtained in about 12% yield. It gives a blue colour with alcoholic ferric chloride showing thereby that it is a C-methyl derivative. It melts at 161–62° and is found to be identical with an aunthentic sample of 2: 6-dimethyl-5-hydroxy-7-methoxy chromone (eugenitin) (II *b*).[12] This result therefore establishes that in the nuclear methylation, the methyl group enters the 6-position of the chromone unit and this preparation also constitutes a new synthesis of eugenitin.



(I)



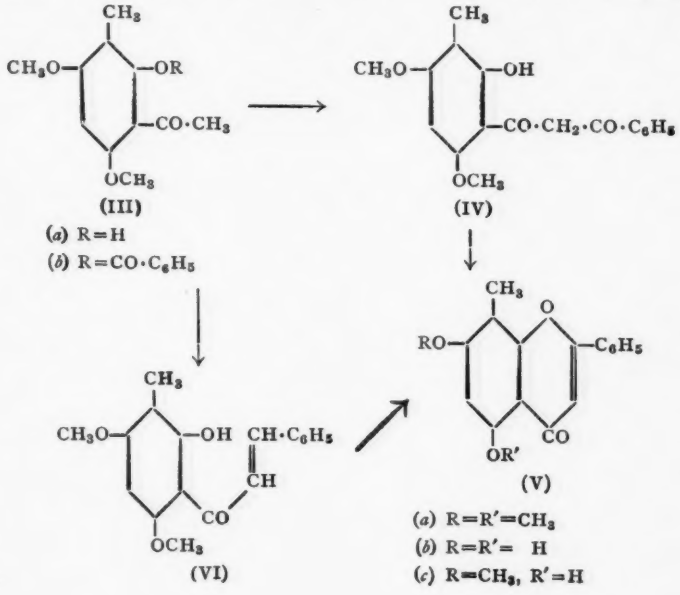
(II)

(*a*) R=H
(*b*) R=CH_3

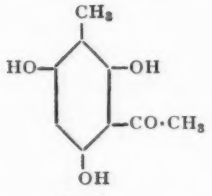
After submitting our preliminary communication on the nuclear methylation of benzo-γ-pyrones,[1] we have come across the note of Whalley[16] in which he has recorded that eugenitin is obtained in an yield of 70% by long heating (12 hours) and by using a very large excess of methyl iodide. We have not been able to obtain this high yield under apparently the same conditions. Actually it is found that the best yield of the C-methyl derivative is obtained by heating the mixture for 4 hours and that longer heating decreases the yield of this product.

As already mentioned the flavone luteolin was subjected to nuclear methylation by Perkin and Horsfall.[4] A more convenient representative of this group is chrysin and it has now been studied for its nuclear methylation. For purposes of comparison authentic samples of 6-methyl chrysin and 8-methyl chrysin were needed. For the preparation of 5: 7-dimethoxy-

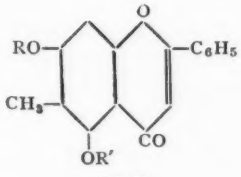
8-methyl flavone (V *a*) the method of Baker and Venkataraman[17, 18] is adopted. The starting point is 2-hydroxy-3-methyl-4 : 6-dimethoxy acetophenone (III *a*)[19] the benzoyl derivative (III *b*) of which gave the intermediate diketone (IV). This could be cyclised to the required flavone (V *a*). The same compound (V *a*) was originally obtained by Lindstedt and Misiorny[15] by the oxidation of 2-hydroxy-3-methyl-4 : 6-dimethoxy chalkone (VI)[20] with selenium dioxide in amyl alcoholic solution. We have also used this method and found that the two products are identical. The demethylation of this substance has been carried out using anhydrous aluminium chloride in benzene solution. The absence of any isomerisation during this demethylation has been established by remethylation with excess of dimethyl sulphate and potassium carbonate in acetone solution whereby the dimethyl ether (V *a*) is again obtained. The demethylated product is therefore 8-methyl chrysin (V *b*). It melts at 255–56° and forms a diacetate (m.p. 182–83°). Partial methylation of (V *b*) with one mole of dimethyl sulphate and potassium carbonate in acetone solution gives rise to 5-hydroxy-7-methoxy-8-methyl flavone (V *c*) (m.p. 234–5°). It gives a greenish blue colour with ferric chloride and a bright yellow sodium salt with aqueous sodium hydroxide solution. The same compound is obtained when excess of methyl iodide is employed in the place of dimethyl sulphate thus proving that under these conditions, methyl iodide does not cause further nuclear methylation.



For the preparation of 6-methyl chrysin, Allan-Robinson benzoylation of C-methyl phloracetophenone (VII) seemed to be suitable. Similar method has been successfully employed for making eugenitol (II *a*) by vigorous acetylation[12]; the hydroxyl group para to the methyl group being more reactive and 6-C-methyl derivative alone seems to be produced. The benzoylation had been studied earlier by Furukawa.[21] He however reported the formation of two products (m.p. 251–52° and 308–10°) and considered them to be 6 and 8-methyl derivatives of chrysin but did not assign any specific constitution individually to each of the products. It is well known that 3-benzoyl flavones are formed in this reaction[22] and no special care seems to have been taken by Furukawa to remove the 3-acyl group. The crude mixture obtained from the reaction has now been subjected to further hydrolysis with 5% aqueous sodium carbonate as originally suggested by Rao, Rao and Seshadri.[23] The resulting mixture has been separated into two sharp melting fractions by crystallisation from alcohol. The more soluble fraction melts at 255–56° and is identical with 8-methyl chrysin (V*b*) described above. The sparingly soluble fraction melts at 308–10° and it should therefore be the isomer, *viz.*, 6-methyl chrysin (VIII *a*). This is in agreement with the general observation that 6-C-methyl derivatives melt higher than the corresponding 8-C-methyl derivatives.[7] Thus in the Allan-Robinson reaction, the behaviour of C-methyl phloracetophenone (VII) is markedly different from what has been met with in the chromone synthesis[12] and in methylation.[19] In these two reactions, the hydroxyl para to the C-methyl group is found to be more reactive than the one present in the ortho position to it. In the flavone condensation both these hydroxyl groups are equally reactive and two products are obtained. An important intermediate in this vigorous acylation may be considered to be the diketone or ω-acyl ketone. The nature of the ω-acyl group would appear to play an important part in the subsequent ring closure.



(VII)

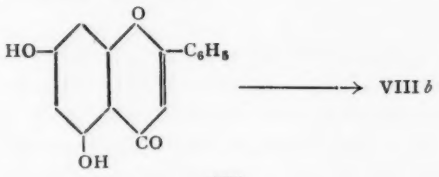


(VIII)

(*a*) R=R′=H
(*b*) R=CH_3, R′=H
(*c*) R=R′=CH_3

On methylation with one mole of dimethyl sulphate and potassium carbonate, 6-methyl chrysin (VIII *a*) yields its 7-methyl ether (VIII *b*). Further methylation has proved to be extremely difficult. By employing a very large excess of dimethyl sulphate in dry acetone solution and by refluxing the mixture for a number of days, this could be accomplished. The resulting dimethyl ether (VIII *c*) melts at 171–72°. The C-methyl derivatives of chrysin and their partial methyl ethers give a bright greenish blue colour with ferric chloride whereas chrysin and tectochrysin give only reddish pink colour. This is parallel to the behaviour of related chromone derivatives, *viz.*, eugenitol, eugenitin, isoeugenitol and isoeugenitin which give a blue ferric reaction whereas noreugenin and eugenin give only a pink ferric reaction (*cf.* Seshadri and Varadarajan[7]).

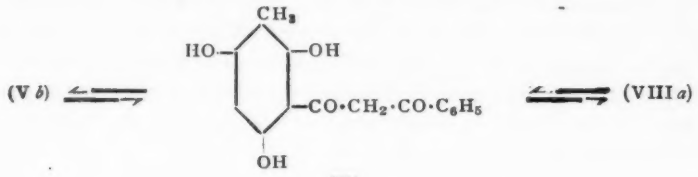
The nuclear methylation of chrysin (IX) has now been carried out under the same conditions as employed in the case of nor-eugenin. The product is obtained in an yield of 10% and is in every way identical with 5-hydroxy-6-methyl-7-methoxy flavone (VIII *b*), thus establishing that in this case also, the methyl group enters the 6-position. The identity has been confirmed by the preparation of the acetates.



(IX)

The results of earlier work on ring isomerism in flavones and chromones brought about by the action of hydriodic acid have already been discussed in an earlier communication.[12] It has been established that 5:7:8-trihydroxy flavones and chromones undergo isomeric change into 5:6:7-trihydroxy compounds on treatment with this reagent. It has also been shown that when 2:6-dimethyl-5-hydroxy-7-methoxy chromone is treated with hydriodic acid, it gives rise to 2:8-dimethyl-5:7-dihydroxy chromone whereas 2:8-dimethyl-5:7-dihydroxy chromone does not suffer isomeric change on heating with this reagent.[12]. In view of the mixture of products obtained in the Allan-Robinson condensation, the behaviour of C-methyl flavones towards this reagent has now been studied. When 5:7-dimethoxy-8-methyl flavone (V *a*) is treated with hydriodic acid, it yields a mixture of products which could be separated into 8-methyl chrysin (V *b*) and 6-methyl chrysin (VIII *a*) by fractional crystallisation. Part of the 8-methyl compound therefore undergoes change into the 6-methyl isomer. 5-Hydroxy-

6-methyl-7-methoxy flavone (VIII *b*) on similar treatment with hydriodic acid yields also a mixture from which both 6 and 8-methyl chrysins could be isolated. Roughly equal quantities are obtained in either of these demethylations. The behaviour of these methyl flavones is therefore markedly different from that of the hydroxy flavones and chromones or even the C-methyl chromones. As already described, even in the flavone ring closure using the Allan-Robinson condensation, both the isomeric methyl chrysins are obtained and hence in both these reactions the hydroxyl groups ortho and para to the methyl group seem to have equal reactivity. An equilibrium seems to exist between the two isomers, the intermediate being the open form, *i.e.*, the diketone (X). This result is rather novel and should be given full consideration in any theory dealing with this subject.



(X)

It should be mentioned here that other reagents also seem to bring about such isomeric change. Lindstedt and Misiorny[15] reported that demethylation of 8-methyl chrysin dimethyl ether with pyridine hydrochloride (6 hours at 200°) yields a mixture from which a small amount of 6-methyl chrysin, produced by partial rearrangement, could be isolated.

In their study of the heart wood components of *Pinus strobus*, after the removal of the two flavanones strobo-pinin and crypto-strobin, Lindstedt and Misiorny[15] isolated from the crude residues a yellow substance which was insoluble in ether (m.p. 285–88°) and had the properties of a flavone with the molecular formula $C_{16}H_{12}O_4$. Only 12 milligrams of the substance were available and using this quantity a careful study was made. The acetate was prepared and was found to melt at 190–91° and alkali fission was carried out and C-methyl phloroglucinol identified as one of the products. It was thus clear that the substance was a C-methyl chrysin with the methyl group in the 6 or in the 8 position.

They also carried out the condensation of C-methyl phloracetophenone with sodium benzoate and benzoic anhydride. From the crude yellowish brown product, they separated out an ether-soluble fraction which after recrystallisation from ethanol yielded yellow crystals melting at 284–88°. Its acetate melted at 190–91° alone or when mixed with strobochrysin acetate.

This fraction was considered to be the same as strobochrysin and hence used as synthetic strobochrysin. When it was fully methylated using excess of dimethyl sulphate and potassium carbonate, a small amount of colourless crystals, m.p. 170–71°, was obtained. It gave no colour with ferric chloride and yellow colour with magnesium and hydrochloric acid. This was different in its melting point and colour reactions from 5: 7-dimethoxy-8-methyl flavone, m.p. 230–31° which as already mentioned was obtained by selenium dioxide oxidation of 2-hydroxy-3-methyl-4: 6-dimethoxy chalkone. Hence it was concluded that strobochrysin was 6-C-methyl chrysin (VIII *a*). Though the data reported in the present paper provide support to their constitution of strobochrysin the melting points recorded by them for the natural flavone (284–86°) and its acetate (190–91°) appear to be too low as compared with synthetic 6-methyl chrysin (308–10°) and its acetate (198–200°) indicating that their samples were not probably quite pure.

Experimental

2-Benzoyloxy-3-methyl-4: 6-dimethoxy acetophenone (III b)

A solution of 2-hydroxy-3-methyl-4: 6-dimethoxy acetophenone (III *a*) (2 g.) in dry pyridine (15 c.c.) was treated with excess of benzoyl chloride (3 c.c.) and the mixture gently refluxed on a wire-gauze for an hour. The mixture assumed a dark red colour after about 30 minutes. It was then cooled and poured into ice-cold dilute hydrochloric acid and stirred vigorously when the reddish brown oily mass that initially separated gradually solidified. The solid product was collected and washed with a small quantity of a mixture of ether and petroleum ether when most of the coloured impurities and the excess of benzoyl chloride were removed. The resulting light pink coloured solid was washed with aqueous sodium bicarbonate solution (5%). It crystallised from alcohol as colourless, stout rhombohedral prisms melting at 132–33°. Yield 2·5 g. (Found: C, 68·4; H, 5·6; $C_{18}H_{11}O_5$ requires C, 68·8; H, 5·7%).

2-Hydroxy-3-methyl-4: 6-dimethoxy dibenzoyl methane (IV)

A mixture of the benzoate (III *b*) (1 g.), powdered sodamide (5 g.) and toluene (15 c.c.) was heated in a boiling water-bath for 6 hours after which the yellow sodium salts were filtered and washed thoroughly with hot dry benzene. When dry, the sodium salts were decomposed by throwing in small lots to ice-water. The yellow solution thus obtained was filtered to remove a small amount of suspended impurities and the clear yellow filtrate was saturated with carbon dioxide. The diketone separated out as an yellow sticky solid and was filtered off. It was crystallised first from a mixture

of benzene and petroleum ether and then from alcohol. It separated as pale lemon yellow thin rectangular plates melting at 127–28°. The compound gives a green colour with ferric chloride in alcoholic solution. Yield 0·5 g. (Found: C, 69·0; H, 5·4; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%.) The same compound was obtained in poor yield by employing potassium carbonate in place of sodamide in the above reaction.

5: 7-*Dimethoxy*-8-*methyl flavone* (*V a*)

The above diketone (0·4 g.) was dissolved in glacial acetic acid (10 c.c.) and heated with fused sodium acetate (1 g.) in a boiling water-bath for 2 hours. It was then cooled and diluted with ice-water when 5: 7-dimethoxy-8-methyl flavone separated out as an yellow precipitate. This was collected and crystallised from alcohol when it came out as pale yellow long narrow rectangular prisms melting at 231–32° alone or when mixed with a sample obtained by the method of Lindstedt and Misiorny.[15] (Found: C, 73·3; H, 5·1; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%.)

5: 7-*Dihydroxy*-8-*methyl flavone* (*V b*)

A solution of 5: 7-dimethoxy-8-methyl flavone (0·6 g.) in dry benzene (35 c.c.) was treated with powdered anhydrous aluminium chloride (2 g.) when the aluminium chloride complex separated out at once. The mixture was heated under reflux in a water-bath for 2 hours and then benzene was distilled off. The residual brownish complex was decomposed with ice and hydrochloric acid and the resulting deep yellow precipitate was collected. It was crystallised twice from ethyl acetate when it came out as deep yellow long rectangular prisms with tapered edges melting at 255–56°. It forms a deep yellow sodium salt with aqueous sodium hydroxide solution and gives a greenish brown ferric reaction in alcoholic solution. Yield 0·45 g. (Found: C, 71·9; H, 4·9; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

The acetate prepared by the acetic anhydride—pyridine method crystallised from alcohol as colourless clusters of rectangular rods melting at 182–83°. (Found: C, 68·1; H, 4·7; $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%.)

Remethylation to (*V a*)

A solution of 5: 7-dihydroxy-8-methyl flavone (0·5 g.), as obtained above, was dissolved in dry acetone (100 c.c.) and treated with dimethyl sulphate (1 c.c.) and ignited potassium carbonate (5 g.) and the mixture refluxed in a water-bath for 30 hours. The solvent was then evaporated and water was added to the residue to dissolve the potassium salts. The mixture was left at room temperature for 2 days to decompose the excess

of demethyl sulphate. The product was then filtered and crystallised from alcohol when it was obtained as pale yellow rectangular prisms melting at 230–31° alone or when mixed with a sample of (V *a*) described earlier.

5-Hydroxy-7-methoxy-8-methyl flavone (*V c*)

To a solution of 5:7-dihydroxy-8-methyl flavone (0·7 g.) in dry acetone (50 c.c.) containing dimethyl sulphate (0·3 c.c., 1·1 mole) was added ignited potassium carbonate (3 g.) and the mixture was refluxed in a water-bath for 4 hours. The solvent was then evaporated and water was added to the residue to dissolve the inorganic salts when a pale yellowish product separated. This was collected and crystallised from a mixture of chloroform and alcohol when it came out as yellow long thin rectangular plates and rods melting at 234–35°. Lindstedt and Misiorny[15] gave the melting point of this compound as 230–31°. It was sparingly soluble in alcohol, acetone and ethyl acetate but easily soluble in chloroform and benzene. It gave a greenish blue colour with ferric chloride in alcoholic solution and was sparingly soluble in aqueous sodium hydroxide solution. (Found: C, 72·4; H, 5·2; $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%.)

The same compound was obtained by using an excess of methyl iodide in place of dimethyl sulphate in the above methylation.

The acetate of the above compound was prepared by the acetic anhydride-pyridine method and was crystallised from ethyl acetate when it came out as colourless short rectangular prisms melting at 208–9°. (Found: C 70·8; H, 5·0; $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9%.)

Allan-Robinson condensation with 3-methyl phloracetophenone

An intimate mixture of C-methyl phloracetophenone (5·0 g.), benzoic anhydride (32 g.) and dry sodium benzoate (6 g.) was heated under reduced pressure at 180–85° for 5 hours. The product was refluxed with alcohol (160 c.c.) for 20 minutes and to the clear solution thus obtained was added a solution of potassium hydroxide (24 g.) in water (25 c.c.) followed by some more alcohol (50 c.c.). The mixture was refluxed for 20 minutes and then the alcohol was distilled off under reduced pressure. Water (500 c.c.) was added to the residue and the solution was filtered and saturated with carbon dioxide. The yellow precipitate was collected, washed and pressed as dry as possible. It was then suspended in aqueous sodium carbonate solution (200 c.c., 5%) and heated under reflux for 2 hours. The mixture was then cooled and filtered to remove a small amount of undissolved matter. The clear filtrate was cooled in an ice-bath and acidified with ice-cold hydrochloric acid. The resulting yellow precipitate was filtered and subjected to

fractional crystallisation from alcohol. The more soluble fraction separated as deep yellow long narrow rectangular prisms with taperd edges melting at 255–56° and a mixed melting point with an authentic sample of 5:7-dihydroxy-8-methyl flavone (V *b*) was not depressed. Yield 1·6 g. Furukawa[21] gave the melting point of this compound as 251–52°. The acetate melted at 182–83° and a mixed melting point with a sample of 5:7-diacetoxy-8-methyl flavone, described earlier, was not depressed. Furukawa[21] gave the melting point of this acetate as 180·5–181°.

The sparingly soluble fraction was obtained in the form of pale yellow tiny rectangular rods melting at 308–10° and this was 5:7-dihydroxy-6-methyl flavone (VIII *a*). Furukawa[21] gave the same m.p. Yield 1·4 g. (Found: C, 71·6; H, 4·5; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%.)

The acetate of 5:7-dihydroxy-6-methyl flavone was prepared by the acetic anhydride-pyridine method and when crystallised from alcohol it was obtained as colourless long silky needles melting at 198–200°. Lindstedt and Misiorny[15] gave the m.p. as 190–91° and Furukawa gives m.p. 196·5-197·5°.

5-Hydroxy-6-methyl-7-methoxy flavone (*VIII b*)

A solution of 5:7-dihydroxy-6-methyl flavone (0·7 g.) in dry acetone (200 c.c.) was refluxed with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (2 g.) for 6 hours. Acetone was then distilled off and water was added to the residue. The undissolved methyl ether was collected, washed with water and crystallised from a mixture of chloroform and alcohol when it separated as very pale yellow long thin needles melting at 171–72°. It gave a green colour with ferric chloride in alcoholic solution. (Found: C, 72·4; H, 5·3; $C_{17}H_{14}O_4$ requires C, 72·4: H, 5·0%). The same product was obtained when excess of methyl iodide was used in the above methylation in place of dimethyl sulphate.

The acetate of the above partial methyl ether was prepared by heating with acetic anhydride and a few drops of pyridine. When crystallised from alcohol twice and then from ethyl acetate, it separated as colourless short rectangular prisms melting at 187–89°. (Found: C, 70·6; H, 4·8; $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9%.)

5:7-Dimethoxy-6-methyl flavone (*VIII c*)

A suspension of 5:7-dihydroxy-6-methyl flavone (0·5 g.) in acetone (75 c.c.) was treated with dimethyl sulphate (4 c.c., excess) and ignited potassium carbonate (10 g.). The mixture was heated under reflux for about 50 hours, more dimethyl sulphate (2 c.c.) and potassium carbonate (4 g.)

being added after 30 hours. The solvent was then evaporated and water was added to the residue to dissolve the potassium salts, when a greenish brown pasty product separated. This was filtered after 24 hours and washed with a little dilute alcohol when coloured impurities were removed and a pale greenish yellow residue was left behind. Crystallisation from dilute alcohol (charcoal) yielded 5: 7-dimethoxy-6-methyl flavone as pale yellow thin rectangular plates melting at 171–72°. Lindstedt and Misiorny[15] gave the same m.p. The product did not give any colour with alcoholic ferric chloride. (Found: C, 72·6; H, 5·4; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%.)

Demethylation of 5: 7-*dimethoxy*-8-*methyl flavone* (*V a*) *with hydriodic acid*

5: 7-Dimethoxy-8-methyl flavone (1 g.) was dissolved in acetic anhydride (25 c.c.) and the cooled solution was treated cautiously with hydriodic acid (15 c.c., d. 1·7). The mixture was heated under reflux in an oil-bath at 140–45° for 2 hours, cooled and poured into ice-water containing some sodium sulphite when a dark coloured precipitate was obtained. This was collected after 2 hours. The product was macerated with a little warm alcohol and filtered again when all the dark impurities dissolved and a yellow residue (0·72 g.) was left behind. This was fractionally crystallised from alcohol when two products were obtained. The more soluble fraction on repeated crystallisation gave 5: 7-dihydroxy-8-methyl flavone (V *b*) melting at 255–56°. It was identical with an authentic specimen described earlier. Yield 0·3 g.

The sparingly soluble fraction was crystallised from a large volume of a mixture of ethyl acetate and alcohol when a pale yellow product melting at 308–10° was obtained. It was identical with an authentic specimen of 5: 7-dihydroxy-6-methyl flavone (VIII *a*) obtained as one of the products of Allan-Robinson condensation of C-methyl phloracetophenone as described earlier. Yield 0·25 g.

Demethylation of 5-*hydroxy*-6-*methyl*-7-*methoxy flavone* (*VIII b*)

5-Hydroxy-6-methyl-7-methoxy flavone was demethylated with hydriodic acid under the same conditions as employed for 5: 7-dimethoxy-8-methyl flavone above. Two products were isolated by fractional crystallisation from alcohol and were identified as 6-methyl chrysin (VIII *a*) and 8-methyl chrysin (V *b*) respectively.

Nuclear methylation of 2-*methyl*-5: 7-*dihydroxy chromone*

2-Methyl-5: 7-dihydroxy chromone (5 g.) was added to an ice-cold solution of sodium methoxide (from 8 g. of sodium) in absolute methanol (200 c.c.) and the resulting dark brown solution was treated with methyl iodide (24 c.c.) which was added all in one lot. The mixture was allowed to stand in the

cold for 15 minutes and then was gently refluxed in a water-bath for 3 hours. Most of the methanol was then distilled off under reduced pressure and the resulting brownish pasty mass was treated with cold water (100 c.c.). The suspension thus obtained was extracted repeatedly with ether. The ether extract was washed once with aqueous sodium hydroxide solution (10%) and then with water. On evaporation of ether, a crystalline solid was obtained which was recrystallised twice from alcohol and then once from ethyl acetate when 2: 6-dimethyl-5-hydroxy-7-methoxy chromone separated as colourless thick prisms melting at 161–62° alone or when mixed with an authentic sample of eugenitin.[12] Yield 0·6 g. It gave a blue colour with alcoholic ferric chloride.

The acetate crystallised from a mixture of ethyl acetate and petroleum ether as thin rectangular plates melting at 176–77° undepressed by admixture with an authentic sample of eugenitin acetate.[12]

Nuclear methylation of chrysin (IX)

To a cold solution of sodium methoxide (from 7 g. of sodium) in absolute methanol (200 c.c.) was added 5: 7-dihydroxy flavone (5 g.) in a finely powdered form and the resulting dark brown solution was treated with methyl iodide (20 c.c.) added all at once. The mixture was gently heated under reflux in a water-bath for 3 hours. Methanol was then removed under reduced pressure and the residual solid was suspended in water (100 c.c.). The mixture was repeatedly extracted with ether containing a small amount of chloroform. The extract was washed once with water, dried (sodium sulphate) and evaporated when a crystalline solid was obtained. This, when crystallised twice from a large volume of alcohol, yielded 5-hydroxy-6-methyl-7-methoxy flavone as pale yellow long thin needles melting at 171–72° alone or when mixed with an authentic sample of the substance described earlier. Yield 0·5 g.

The acetate crystallised from alcohol as colourless rectangular prisms melting at 187–89° alone or on admixture with an authentic sample of 5-acetoxy-6-methyl-7-methoxy flavone described earlier.

SUMMARY

Nuclear methylation of nor-eugenin (2-methyl-5: 7-dihydroxy chromone) and chrysin has been carried out. It takes place in the 6-position. The former yields eugenitin (2: 6-dimethyl-5-hydroxy-7-methoxy chromone) and the later yields 6-methyl tectochrysin. For the synthesis of reference compounds several methods have been examined and anthentic samples of 6 and 8-methyl chrysins and their derivatives obtained. It is found that Allan-

Robinson condensation of 3-methyl phloracetophenone and benzoic anhydride yields a mixture of 6 and 8-C-methyl chrysins. Further, hydroiodic acid demethylation of the methyl ethers of each of these C-methyl chrysins again gives rise to a mixture of these C-methyl chrysins. In both these reactions the yields are almost equal. Aluminium chloride in boiling benzene solution does not produce isomeric change. The results of present work support the structure of strobochrysin proposed by Lindstedt and Misiorny.[15]

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EFFECT OF DETERGENTS ON THE ACTIVITY AND INACTIVATION OF INVERTASE

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Introduction

It is well known that the activity of sucrase is affected by cations and cationic dyes.[1] It is of interest to examine how detergents influence the activity and also how acids and alkalies inactivate sucrase.

Experimental

1. *Materials*

(*a*) *Sucrase.*—The sample of sucrase used was the same as has already been described.[2]

(*b*) *Detergents.*—(i) Cerefak; Alkylated aromatic hydrocarbon sulphonate. The Alkyl group is a mixed dodecyl radical. (ii) Fixanol C (I.C.I.): Consists of cetylpyridinium bromide. (iii) Lauryl compound; Lauryl paratoluidine disodium sulphonate. This was kindly supplied in the pure form by Dr. K. Venkataraman, Director, Department of Chemical Technology, Bombay University, Matunga, Bombay. (iv) Detergent 40 A: Supplied by Standard Vacuum Oil Co. (v) Sandopan N and (vi) Sandofix LW: Proprietary reagents used as textile auxiliaries.

(*c*) Chemicals used were of reagent or analar quality of Merck or B.D.H.

2. *Technique for the determination of the effect of detergents on the activity of sucrase at pH* 4·5.

Our sucrase preparation had a time value of 58 minutes per c.c. In the present work we have taken arbitrarily the activity of the sucrase present in 1 c.c. of this preparation as 100 units. We have measured the activity of other products dealt with in this paper in terms of this arbitrary standard.

The principle of the method consists in finding out the number of milligrams of invert sugar produced by different quantities of the stock solution by following a special experimental procedure. 10 c.c. of 20% sugar solution is taken in a large diameter tube which is kept in a thermostat at 25° C.

To this are added 7 c.c. of acetate buffer pH 4·5 and (8-X) c.c. of distilled water and X c.c. of sucrase preparation under test. The mixture is kept at 25° C. for 5 minutes and then the reaction is stopped by adding excess of N/4 caustic soda solution, final pH 11. The solution thus obtained is made up to 250 c.c. in a measuring flask. 5 c.c. of this dilute solution are withdrawn and added to 5 c.c. of copper reagent or a multiple of this volume contained in a large tube. After mixing the solutions the tube is placed in boiling water and heated for 15 minutes. The tube is then cooled quickly by immersing in ice-cold water. 2 to 3 grams of potassium iodide is then added to it and the solution is acidified by 2 M sulphuric acid. After waiting for five minutes the liberated iodine is titrated against 0·1 N sodium thiosulphate. The total copper in 5 c.c. of copper reagent is determined by a second titration with the copper reagent only. The difference between the two titration results is equivalent to cuprous oxide precipitated by reducing sugar. Each c.c. of the difference indicates 6·36 milligrams of copper. The corresponding amount of reducing sugar is found from Munson and Walker tables.[3] A graph is then constructed by plotting the number of milligrams of invert sugar produced against the number of arbitrary units of sucrase used. The activity of any other solution of sucrase can then be found out by determining the milligrams of invert sugar produced and referring to graph.

A 2·5% solution of sucrase concentrate (1 c.c. = 100 units) is made in acetate buffer of pH 4·5. To this is added the necessary quantity of the commercial detergents so as to make the final solution correspond to 0·2% or 0·5% with respect to the detergent. The solution is kept at 25° C. for 5 minutes and then 10 c.c. sample is taken and its activity determined as has already been described.

3. *Examination of the effect of the detergents on the kinetics of inactivation of sucrase.*

The procedure for examining the kinetics of inactivation of sucrase at low pH is the same as followed previously.[4] These experiments have been repeated with solutions containing some of the commercial detergents at different concentration and different pH. The results are given in Tables II, III and IV.

Discussion

1. *Effect of detergents on the activity of sucrase at pH* 4·5

It is found that the detergents are effective in lowering the activity of sucrase. The cationic detergents are much more effective than the anionic

ones as can be easily seen from Table I. The lowering of activity is presumably connected to the formation of complexes between the detergents

TABLE I

Effect of Detergent on the Activity of Sucrase

No.	Detergent	% concentration of the detergent	% reduction of activity
1	Lauryl compound ..	0·5	10·0
	do ..	0·2	5·7
2	Cerefak ..	0·5	11
	do ..	0·2	5·9
3	Fixanol C ..	0·5	44·4
	do ..	0·2	11·5
4	Detergent 40 A ..	0·5	15·5
	do ..	0·2	9·9
5	Sandopan N ..	0·2	3·8
6	Sandofix LW ..	0·2	50·0

and the enzyme. This complex formation might indeed be caused by the union of the hydrophobic group of the detergent with the hydrophobic group of sucrase. In the case of Sandofix LW this appears to have been caused at least partly by the copper salt present in the detergent.

2. *Effect of detergents on the critical pH region of inactivation*

It has been shown in an earlier paper that the rate of inactivation of sucrase is a function of pH. When the extent of inactivation was measured by subjecting sucrase to different pH values for a constant period of 5 minutes, it is found that at a pH of 1·8 or lower, the inactivation rose to 100%, whereas at 2·3 or higher pH values there was practically no inactivation.[5] It may therefore be taken that 1·8 to 2·3 represents a critical pH region at which the sucrase passes from practically stable to a highly unstable state. An examination of Table II shows that in the presence of 0·1% cerefak also there is an exhibition of a similar pH range. The range however is 3·0 to 3·4. The effect of cerefak therefore appears to be to shift the critical pH range to higher regions of pH.

The question arises as to what is the cause of this shift of the critical pH range. Whereas the elucidation of the exact cause of it should await the collection of further extensive data, it is proposed to discuss one of the possible

TABLE II

Effect of 0·1% *cerefak on the inactivation of sucrase when subjected to different pH for* 5 *minutes at* 25° *C.*

pH to which sucrase is subjected	Percentage reduction of activity due to 0·1% cerefak
2·8	100
3·0	100
3·4	75
4·5	2·6
6·3	4·7
7·0	14·0
8·5	100
10	100

factors presumably responsible for the effect. It is known that cerefak contains within it a hydrophobic and hydrophilic group. This is also the case with sucrase as can be seen from the facts (*a*) it spreads on aqueous substrata,[6] (*b*) the solution gives fairly stable foam and (*c*) the solution affects the dropping mercury electrode capacity.[7] Whenever two surface-active substances co-exist in solution there is a chance of formation of complexes between the two types of molecules. This complex formation is caused by the attractive force between the hydrophobic parts of the molecules of the two types of the surface-active substances. This is responsible for the errors caused in the indicator method of pH measurement, by the presence of detergents.[8] The surface-active substance produces an apparent shift of pH. This is attributed to the indicator sticking to the surface-active agent ion and indicating the pH of the ion atmosphere of the surface-active ion. That this effect is also shown by cerefak was confirmed by measuring the apparent pH shift produced when the pH of the buffer is measured by thymol blue. These measurements have been made by Gillespie method using D.G. Spectrophotometer for measuring the colours of acid and basic standards as well as test solution.[9] It is clear from the above work that the pH of the ion atmosphere of cerefak is lower than the bulk pH and the average pH shift due to this effect can be as high as 1·5 units. It is just possible that the shift of the critical pH range for inactivation of sucrase is also due to

the sucrase taking up the detergent molecules and experiencing a high hydrogen-ion concentration due to the ion atmosphere of the detergent ions. This explanation can also hold in the case of Lauryl paratoluidine disodium sulphonate (*vide* Table III) which is also an anionic detergent.

TABLE III

Effect of lauryl compound on the inactivation of sucrase in 5 minutes at 25° C.

pH to which the sucrase is subjected	Percentage reduction of activity	Concentration of lauryl compound
		%
2·5	100	0·1
3·0	53·6	0·1
4·5	5·7	0·2
4·5	10·0	0·5

Whereas the above hypothesis is intellectually very satisfying its correctness can be proved by cationic detergents which should be expected to shift the critical pH range to lower values. The only cationic detergent tried so far is Fixanol C (*vide* Table IV). The table shows that the cationic detergent instead of shifting the critical pH region to higher values renders sucrase more unstable. Further work with other cationic detergents will be of interest from this point of view.

TABLE IV

Effect of Fixanol C on the inactivation of sucrase in 5 minutes at 25° C.

pH to which sucrase is subjected	Percentage reduction of activity in presence of 0·2% Fixanol C	Percentage reduction of activity in absence of Fixanol C
1·0	100	95
2·5	66	c.a. 7
3·0	16	c.a. 7
4·5	12	0

Summary

1. Detergents are shown to decrease the activity of sucrase.

2. The cationic detergents are found to be more effective than the anionic detergents.

3. The critical pH region of inactivation of sucrase is found to shift to higher pH values in the presence of anionic detergents.

4. A provisional explanation based on the Debye ion atmosphere concept has been put forth and the limitations of the hypothesis discussed.

Acknowledgments

The author wishes to express his most sincere thanks to Professor K. S. G. Doss, D.Sc., F.R.I.C., F.A.Sc.,F.Inst.P., Head of the Department of Chemistry, Indian Institute of Sugar Technology, Kanpur, for his able guidance and discussions. Thanks are also due to Professor J. M. Saha, Director, Indian Institute of Sugar Technlology, for his kind interest in the work.

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STUDIES ON SOUTH INDIAN RADIOACTIVE MINERALS

II. Allanite from Madura

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Received April 8, 1953
(Communicated by Prof. C. Mahadevan, F.A.SC.)

Abstract

Allanite, a cerium-bearing epidote occurring in the pegmatites of Kavarkattumalai, Madura District, has been studied in detail. The investigations comprise the determination of physical and optical characters, chemical composition, mineral formula, and autoradiographic studies. Attempts have been made from a study of the data on metamict and non-metamict allanites to formulate the changes that allanite undergoes when it becomes metamict. Evidence has been collected to show that the allanite from Madura had become metamict and is hence of dubious value as an age index.

Introduction

Muthuswami[8] reported the occurrence of allanite in the pegmatites intrusive into the Archæans of Kavarkattumalai, Madura District, and this discovery opened up a new source of data to determine the sequence of Peninsular Archæans. The Archæans in this area consist of bands of quartz-magnetite rocks, garnetiferous biotite gneisses, norites and pyroxenites. As the contemporaneity or otherwise of this group of rocks with their counterparts in the coastal Circars and Mysore has long been in question, an attempt has been made to solve the problem by dating the Madura pegmatitic cycle and interpreting it with the available geo-chronological evidence.

Experimental and Results

Physical Characters

The specific gravity of the mineral is 3·63. The specimen is roughly tabular and is probably parallel to (100). Lustre is sub-metallic. Colour is black. Fragments from the core of the mass are velvety black and lustrous but the outer portions are dull black in colour. The allanite is traversed by a small vein of a different mineral, which stands in contrast by its very pale yellow colour. Small flakes of mica can be seen adhering to the mineral.

Optical Characters

The mineral has a brownish yellow body colour and is pleochroic. It is traversed by a network of cracks in the major portion of the section. Adjacent to the region where parallel cleavages are developed, the mineral changes to a colourless one with an extinction angle of 10°. It is significant that the cleavage systems in the two cases are similarly oriented. This associated mineral is most probably clinozoisite.

The clinozoisite shows the presence of bright red ochery material. The deposition of this material appears to have been effected through the cleavages, as the latter have a reddish border running adjacent to them and terminating in lumps of ochery material. There are inclusions, presumably solid, in allanite, which are systematically spaced.

Chemical Composition

The mineral was chemically analysed by the well-known methods of Schoeller and Powell[11] and A. F. Williams.[12] The methods used in the estimation of rarer elements are briefly described below.

(1) *Thorium.*—The mineral is fused with KOH and treated with dilute hydrochloric acid. The rare-earths and thorium are separated by double oxalate precipitation and finally thorium is isolated from rare earths by precipitation with potassium iodate, converted into oxalate, ignited and weighed as ThO_2.

(2) *Cerium and Yttrium Earths.*—The rare earths are precipitated as oxalates in the hydrochloric acid medium. A broad separation between cerium and yttrium earths is effected by double sulphate precipitation. Cerium is separated from cerium-earths by potassium iodate procedure.

The values for the various constituents are recorded here, along with values given by other workers for Allanite.

It appears from the analytical data that the mineral is similar to the specimen from Llano County, Texas, studied by Marble.[5]

A variation graph has been drawn on the basis of the analytical data, which are relatively modern and more reliable. The author's results have been plotted on the graph and they have been found to be within the limits.

Autoradiographic Studies

The autoradiograph was obtained for allanite by exposing it for 35 days, as suggested by Marble. The following observations have been made:

TABLE I

	A	B	C	D	E
SiO_2 ..	30·12	32·20	30·42	33·73	29·89
Al_2O_3 ..	18·06	17·18	17·00	16·09	19·09
FeO ..	7·62	10·38	11·96	3·87	8·49
Fe_2O_3 ..	8·03	3·79	5·45	10·68	6·41
TiO_2 ..	0·70	0·74	..	0·80	0·89
MgO ..	0·14	0·69	..	0·18	0·15
CaO ..	9·60	11·95	13·38	16·18	8·48
SrO ..	..	n.d.	..	..	..
MnO ..	0·72	0·26	0·80	0·06	..
ThO_2 ..	1·56	1·05	2·37	..	0·82
Ce_2O_3, La_2O_3 ..	20·21*	18·30	16·40	15·55	22·55
Y_2O_3 ..	0·97*	0·72	1·42	1·10	0·81
U_3O_8 ..	..	..	..	..	..
P_2O_5 ..	n.d.	..	..	..	..
Na_2O+K_2O ..	0·12	0·02	..	..	0·24
PbO ..	n.d.	..	..	..	..
H_2O ..	1·90	2·18	0·73	1·69	1·84
	99·75	99·46	99·93	99·93	99·66

* Uncorrected for peroxidic oxygen.

A. Metamict allanite from Madura.
Analyst: Aswathanarayana, U.

B. Allanite from Wilmot Pass, Fiordland, New Zealand.
Analysts: Seelvye and Hutton.[3]

C. Allanite from Madagascar.
Analyst: Carrobi.[3]

D. Allanite from Michalkowo (Russia).
Analyst: Kostov.[3]

E. Allanite from Barringer Hill, Llano Country, Texas.
Analyst: J. P. Marble.[5]

(*a*) Inclusions are present but their distribution appears to be sporadic and confined to the border zones of the mineral.

(*b*) A number of irregular cracks are present which might have facilitated the processes of leaching and enrichment.

(*c*) The outer rim of the mineral shows a high photographic density which, as a rule, is associated with higher radioactive content. This is indicative of the leaching of the mineral, resulting in the segregation of a mineral, richer in radioactivity, towards the periphery of the mineral. Most likely the secondary mineral may be gummite or one belonging to that group.

Discussion

Nature of Association.—Muthuswami,[8] who has reported the occurrence of Madura Allanite, did not record the existence of any other rare earth mineral in association with Allanite. On the strength of the theoretical work of Quirke and Kremers[10] on the associational aspects of rare earths, it may be said wherever Allanite is found, " more rare earths might have combined with most, if not all, of the phosphate in the magmatic solutions and hence may be found as Monazite in the higher temperature phases of the same rock assemblage." Thus it can be reasonably presumed that Monazite may be found somewhere in the vicinity of the recorded occurrence of allanite. It is suggested that it is not unlikely that the transition may be effected through Nagetelite, a silicate and phosphate of rare earths and a member of the epidote group.

Under the microscope, the mineral shows the association with clinozoisite. The epidote group to which both allanite and clinozoisite belong forms an isomorphous series and both allanite and clinozoisite can be derived by simple replacement of constitutent elements—monovalent Ca by Fe and trivalent Al by Fe. Both of them are monoclinic. Thus the association of allanite and clinozoisite is quite understandable. The transition between allanite and clinozoisite is apparently sharp. In some regions allanite has developed a lighter colour in comparison with the deep colour of the rest of the section and this concides with the development of cleavage system, parallel to that of clinozoisite. This suggests that probably these small patches have effected the transition from allanite to clinozoisite.

Formula.—There appears to be considerable diversity of opinion regarding the usage of terms orthite and allanite. " The term allanite was originally intended to denote those small unaltered crystals that were tabular parallel to the orthopinacoid, whereas orthite was reserved for large crystals of prismatic habit, whose analyses showed a considerable degree of hydration and leaching."[3] Hutton[3] recently discussed the nomenclature adopted by Lokka, Mountain, Simpson, Marble and Geijer and expressed himself in favour

of abandoning the term orthite, and using allanite to signify the cerium-bearing members of the epidote group, without regard to the crystal habit or degree of metamictisation—a view which is bound to be popular in view of its simplicity of approach.

Nandi and Sen[9] have recently presented the various formulæ suggested for allanite by Groth, Marble, Takuba and Yukawa. The monoclinic members of the epidote group of which allanite is one, are believed to form a solid solution series. The role of the hydroxyl, ferric and ferrous radicals and the nature and extent of molecular replacements among the elements involved appear to be responsible to the discordance in the chemical formulæ suggested for allanite.

Winchell[13] is uncertain whether allanite and other minerals of the epidote group have frame works of (Si, Al) O_2 or not, but suggests they have to be provisionally placed in that group for lack of more accurate data.

The author suggests the following formula on the basis of his analytical results: 5 AO.2 B_2O_3.2H_2O. 9SiO_2, where A = Fe″, Mn, Ca, Mg; B = Ce, Y, Fe‴, Al. Another arrangement has been worked out, grouping Ca and Ce on the basis of the similarity of their ionic nucleii and this has given a formula: 2 (Ca, Ce) O, 3 (Al, Fe, Y, Mn, Mg) O, 5 SiO_2.H_2O.

Metamictisation of Allanite

The following evidence is adduced to show that Madura allanite had become metamict:

(1) The appreciable H_2O content (1·9%) which the mineral exhibits is generally associated with alteration and hydration.

(2) The low specific gravity of the mineral (3·63) is of the same order as that recorded by Marble[5] for the metamict allanite from Barringer Hill, Texas (3·54). It is clearly different from the anisotropic varieties with a specific gravity of 4·0. The low specific gravity of Madura Allanite can be expalined to have resulted from the leaching of heavier elements like Ur, Th and rare earths and introduction of water.

(3) The low refractive index[8] is particularly significant. Most of the anisotropic fresh allanites gave a refractive index of $1·80 \pm 0·02$, while the metamict types gave an R. I. of $1·70 \pm 0·01$.

(4) The isotropy of the allanite is indicative of its alteration. The original anisotropic mineral gradually gets altered and becomes isotropic, as has happened in the case of Madura allanite. A few anisotropic specks here and there, observed in this case, do not alter the situation appreciably.

(5) *Effect of Concentrated HCl.*—The mineral undergoes rapid decomposition when treated with small quantities of hot concentrated HCl and the resulting solution rapidly sets into a jelly. This behaviour compares favourably with that noted by Osborne Hutton in the case of metamict allanites from Albany, Wyoming and Barringer Hill, Texas.

The significance of this property of Madura allanite can be best appreciated, when contrasted with the behaviour of non-metamict and fresh allanites on similar treatment. An extreme case is the allanite from Wilmot Pass, New Zealand,[3] which has been found to decompose only after the most drastic treatment, *i.e.*, prolonged heating with fuming sulphuric or perchloric acids. The Yosemite Park allanite, however, is readily soluble in hot concentrated hydrochloric acid, with the separation of pulverent silica, which does not set into a jelly. It may be mentioned, by the way, that this conspicuous difference in the behaviour of two types of non-metamict allanites has been found to be dependent upon whether the octahedral positions in the lattice are dominantly occupied by aluminium or by iron and/or manganese.[2]

The author has made a critical study of the data on metamict and non-metamict allanites occurring all over the world and suggests the following differences between metamict and non-metamict allanites:

	Metamict	*Non-metamict*
1. H_2O content ..	High ($1 \cdot 8 \pm 0 \cdot 2\%$)	Low ($0 \cdot 9\%$)
2. Refractive index ..	Low ($1 \cdot 69 \pm 0 \cdot 01$)	High ($1 \cdot 80 \pm 0 \cdot 02$)
3. Optical characters ..	Isotropic	Anisotropic
4. Specific gravity ..	Low ($3 \cdot 5 \pm 0 \cdot 1$)	High ($4 \pm 0 \cdot 1$)
5. Action with HCl ..	Readily decomposes on treatment with hot conc. HCl and rapidly sets into a jelly.	Some decompose relatively easily but with the separation of pulverent silica. Others decompose only with difficulty on treatment with sulphuric and perchloric acids.

Autoradiographic Studies

The autoradiograph of allanite is suggestive of the alteration it has undergone, thus making the mineral useless as an age-index. The processes of leaching have taken place to an unknown extent.

Conclusion

A study of the physical and optical characters, chemical composition and behaviour on the addition of concentrated hydrochloric acid, distinctly

points to the conclusion that Madura allanite had become metamict and hence is of dubious value, if not useless, as an age-index. Such a situation precludes the possibility of dating the Madura pegmatitic cycle which, when interpreted with the ages of other pegmatitic cycles, would have given us a clearer picture of relative positions of Peninsular Archæans.

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I wish to place on record my deep sense of gratitude to Professor C. Mahadevan, for his continued interest and encouragement during the progress of work. I am thankful to C.S.I.R. for their financial assistance. My thanks are also due to Professor T. N. Muthuswami for having kindly sent the allanite specimen.

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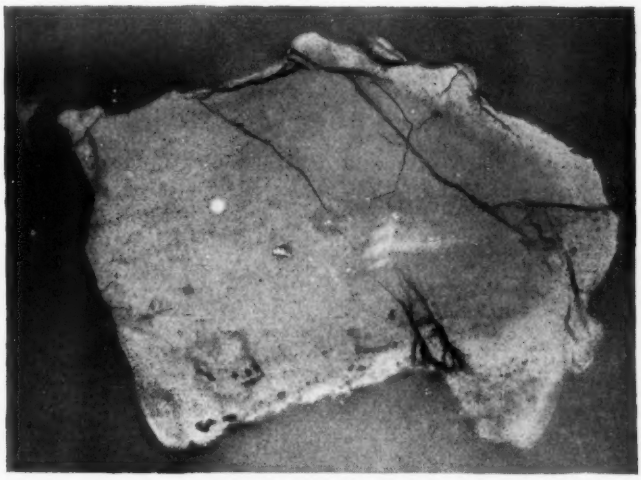
ALLANITE



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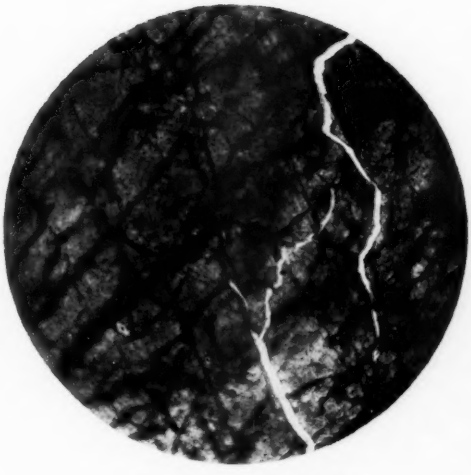

MICROPHOTOGRAPH

RAMAN EFFECT IN MIXTURES OF BENZALDEHYDE WITH ALCOHOLS AND PHENOL

Hydrogen Bond Formation

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Received May 30, 1953

(Communicated by Prof. S. Bhagavantam, F.A.SC.)

1. Introduction

In an earlier communication by the author (1953), Raman spectra in mixtures of acetone with alcohols have been studied. It was found that the diminution of C = O frequency in acetone due either to hydrogen bond formation or to certain other changes in chemical constitution is always accompanied by a corresponding increase in the C—C frequency, suggesting that the vibrations of the whole group C—C—C are to be regarded as affected thereby

and not of the C = O linkage alone. Such investigations have been extended by the author to other Ketones as well and the results obtained furnish further evidence in support of the new ideas that have been put forward. Details will be published in due course but in the Plate accompanying this paper, a picture of benzophenone with arrow marks on the lines that are shifted, is reproduced. In continuation of that work it is programmed to study a few aldehydes as well and the results obtained in mixtures of benzaldehyde with alcohols and phenol are now given with a view to bring out similar effects due to hydrogen bond formation, this time on the group C — C — H, one of the carbons being in the benzene ring itself.

Murty and Seshadri (1942) studied the Raman spectrum of the mixture of benzaldehyde and phenol and reported a diminution of C = O frequency from 1698 cm.$^{-1}$ to 1670 cm.$^{-1}$ Their attention was, however, confined only to the C = O link because of its direct bearing on the hydrogen bond formation. Besides, the data published by them do not contain information regarding the concentrations of the mixtures studied.

2. Experimental

Benzaldehyde has been purified by repeated distillation at constant boiling point of 179° C. Phenol has been purified by the usual process of

distilling, allowing it to solidify by cooling the distilled matter and absorbing the moisture. By a repetition of this process, pure colourless phenol crystals are obtained. Fuess glass spectrograph and a Hilger's Raman Source Unit are used to record the spectra. Intense and complete Raman spectra of benzaldehyde could be obtained in 20 minutes. With mixtures containing the scattering liquid only as a fraction, proportionate time is allowed for the exposures. In the case of benzophenone, an exposure of a few seconds reveals practically all the prominent lines. On account of such quick exposures, the aldehyde or the phenol or benzophenone do not get coloured which would have been the case if prolonged exposures had to be used.

3. RESULTS WITH PURE LIQUIDS

The Raman frequencies of benzaldehyde and phenol, as obtained by the author are given below:

(1) *Benzaldehyde*

135 (6 *b*), 250 (2), 436 (6 *b*), 611 (6), 644 (2), 824 (8), 993 (10), 1017 (3), 1159 (5 *b*), 1197 (9), 1292 (8 *b*), 1378 (0 *b*), 1448 (0 *s*), 1493 (1 *d*), 1591 (10), 1641 (3 *d*), 1694 (10), 3060 (3).

(2) *Phenol*

240 (2), 504 (1), 532 (2), 620 (4), 750 (2), 812 (2), 826 (2), 1000 (10), 1028 (6), 1064 (0), 1160 (4), 1170 (3), 1258 (2), 1592 (8), 1601 (2), 3014 (1), 3046 (5), 3060 (10).

In all the spectrograms of benzaldehyde, the relative intensities of the lines 1159 cm.$^{-1}$ and 1197 cm.$^{-1}$ do not conform to the results reported by earlier workers. Kohlrausch and Pongratz (1934) record them as having equal intensities, and Murty and Seshadri (1942) estimate them as 10 and 8. A broad band at 1641 $\pm$ 10 cm.$^{-1}$ is now recorded for the first time and it appears to be an overtone of 824 cm.$^{-1}$

4. IDENTIFICATION OF GROUP FREQUENCIES

In Table I are given the important frequencies of benzene and some of its derivatives.

We need not comment on the assignment of the well known frequencies of the benzene ring which are easily recognisable in the above table. The first point of interest is the presence of 1209 in toluene, 1197 in benzaldehyde and 1190 in benzonitrile. This may, therefore, be regarded as arising from the C—C linkage between the ring carbon on the one hand and the aliphatic

TABLE I

Important Raman Frequencies of Benzene and Some of Its Derivatives

1. Benzene C_6H_6	605	849	991	1178			1584 1606		2947	3060
2. Toluene $C_6H_5CH_3$	622	786	1002 1029	1154	1209	1430	1604		2920	3054
3. Benzaldehyde C_6H_5CHO	611	824	993 1017	1159	1197	1448 1493	1591	1694		3063
4. Benzonitrile C_6H_5CN	619	754	998	1175	1190		1595			3063

carbon on the other. Similarly 1430 in toluene and 1448 and 1493 in benzaldehyde suggest that they are due to transverse oscillations of the aliphatic C—H linkage. Their absence in benzene and benzonitrile is naturally to be expected. A frequency due to the longitudinal oscillation of the aliphatic C—H, like the 2920 of toluene, should have appeared in benzaldehyde but has not appeared.

Therefore, the frequencies of benzaldehyde which we may associate with the group C—C—H are 1197, 1448, 1694 with the probability that a
1493
‖
O
frequency in the neighbourhood of 2940 has not been observed.

5. RESULTS WITH MIXTURES

Methyl, ethyl and *n*-propyl alcohols are chosen for studying the effect of their admixture with benzaldehyde.

In the case of methyl alcohol mixture, from 100% benzaldehyde, the concentration of the aldehyde is reduced to 10% by volume, by gradual steps, care being taken to use freshly distilled aldehyde every time. In the 50: 50 mixture, there is a slight shift of 1694 cm.$^{-1}$ line towards shorter frequency. When the concentration of the aldehyde is reduced to 20% by volume, the phenomenon of critical opalescence is observed. The intensity of the Rayleigh lines becomes so great that there is a general blackening of the spectrum.

The admixture of ethyl alcohol with benzaldehyde does not affect any of the frequencies of the aldehyde, but strong opalescence sets in when the concentration of the aldehyde is reduced to 20% by volume.

The mixing of propyl alcohol does not produce any effect whatsover.

Raman frequencies of the mixtures of benzaldehyde and phenol which show displacements with varying concentrations are given in Tables II (*a*) and II (*b*). In Table II (*a*) the variations of the low frequencies of benzaldehyde are recorded. With the increase of the phenol content of the mixture, the Raman line at 135 cm.$^{-1}$ shifts to a marked extent and reaches 151 cm.$^{-1}$ at high concentrations. In Table II (*b*), variations in respect of the two higher frequencies are given.

TABLE II (*a*)

Low Frequencies of Benzaldehyde in Mixtures with Phenol

	Pure Benzaldehyde	0·87 : 1 mol. of phenol / mol. of aldehyde	1·81 : 1 mol. of phenol / mol. of aldehyde	2·92 : 1 mol. of phenol / mol. of aldehyde	3·98 : 1 mol. of phenol / mol. of aldehyde
1	135	143	139	145	151
2	233	238	243	..	247
3	436	442	437	447	..

TABLE II (*b*)

Frequencies of the $C-\overset{\overset{O}{\|}}{C}-H$ *Group*

Link	Pure Benzaldehyde	0·87 : 1 mol. of phenol / mol. of aldehyde	1·81 : 1 mol. of phenol / mol. of aldehyde
C – C	1197	1201	1204
C = O	1694	1684	1680

The shifts in case of all the above frequencies marked with arrows in the figure, are easily noticeable and quite marked.

6. DISCUSSION OF THE RESULTS

Table II (*b*) shows the outstanding feature of this investigation that while the C = O frequency decreases, the C — C frequency increases. This effect is similar to the one noticed by the author in acetone mixtures and

suggests that the hydrogen bond formation has its effect on the aldehydic group as a whole and not merely on the C = O linkage.

As in acetone, the same phenomenon is seen to occur again when the carbonyl frequency is lowered, by an altogether different process, such as the substitution of one of the hydrogens in the ring by a suitable group. The Raman frequencies of C — C and C = O linkages in a few substituted aldehydes, studied by earlier workers, and illustrating the above point are given below in Table III.

TABLE III

Raman Frequencies in Some Substituted Aldehydes

Name of the aldehyde	Formula	C — C Frequency cm.$^{-1}$	C = O Frequency cm.$^{-1}$	Investigator
1. Benzaldehyde ..	C_6H_5CHO	1201	1696	Kohlrausch and Pongratz (1934)
2. O. Chloro-benzaldehyde	Cl-C_6H_4-CHO	1262	1682	Bonino and Ansidei (1934)
3. Salicylaldehyde ..	OH-C_6H_4-CHO	1230	1663	S. Venkateswaran and S. Bhagavantam (1930)

The data given in Table III show that the diminution of the C = O frequency is accompanied by an enhancement of the C — C frequency.

In the case of acetone and alcohol mixtures, an increase in the C — H frequency has been noticed. In the benzaldehyde spectrum the two lines due to the C—H linkages in the aldehyde group—1448 cm.$^{-1}$ and 1493 cm.$^{-1}$ —are very weak and as such, variations in their frequencies could not be measured.

The author expresses his sincere thanks to Professor S. Bhagavantam for suggesting the problem and giving necessary guidance.

7. SUMMARY

The 1197 cm.$^{-1}$ line in benzaldehyde is attributed to the C—C linkage between the aldehyde and the phenyl groups. The admixture of methyl and ethyl alcohols does not affect the C—C and C = 0 frequencies in benzaldehyde. Mixtures with phenol show the formation of hydrogen bond resulting in the weakening of the C = O link and a lowering of the relative frequency.

This is accompanied by an increase of the C—C frequency in the group C—C—H. This phenomenon is analogous to what has been observed when
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O
hydrogen bonds are formed between acetone and alcohol molecules.

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Raman Spectra

FIG. I. (*a*) Pure benzaldehyde, (*b*) benzaldehyde with phenol

FIG. II. (*a*) Benzophenone in CCl_4, (*b*) benzophenone with phenol

ANISOTROPIC BEHAVIOUR OF ROCKS

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(Communicated by Prof. C. Mahadevan, F.A.SC.)

1. Introduction

The variation of elastic properties of rocks with direction has been studied by Zisman (1933), Ide (1935), Birch and Bancroft (1938), Prasadarao (1947) and Sundararao (1948). Zisman used a static method and determined the Young's modulus of several rocks in different directions and found that the variation of Young's modulus with direction is large in certain rocks like Vermont Marble, Layered Gneiss and Limestone. On the other hand, perfect isotropy is found in Vinal haven trap and in Quincy Granite. According to him, it should not however be concluded that only layered or bedded rocks show great anisotropy, for French Creek Norite is decidedly anisotropic. He later measured the linear compressibilities of the rocks along three mutually perpendicular directions using a piezometer devised by Bridgman (1931) and his results show departures from isotropy. Working with Zisman's specimens themselves, Ide has determined the Young's modulus of those rocks by a dynamic method. His results show little difference between the direction parallel and perpendicular to foliation. This is confirmed further, by the values of the modulus of rigidity obtained by Birch and Bancroft by a dynamic method. Prasadarao working on some Indian rocks showed that there is marked anisotropy while Sundararao observed that ultrasonic velocity remains the same in three mutually perpendicular directions, in the case of Quartzite, indicating perfect isotropy. These conclusions, which are somewhat discordant, seem to indicate that in certain rocks, even though static methods yield results exhibiting anisotropy, dynamic methods may yield results showing isotropy. Against this background, it is thought desirable to study the variation of ultrasonic velocity with direction in some Indian rocks, and the results obtained by the author are given in this paper.

2. Description of Rocks

Quartzites, Marbles and Granites of Hyderabad State have been studied. Thin sections of these rocks are cut in different directions and are studied under the microscope for a detailed examination of mineralogical and

textural features of the rocks along with the degree of compactness, and a brief description is given below.

Quartzite A.—This quartzite has been taken from Yellandulapadu in the Warangal District (Hyderabad) included in the Survey of India Topo Sheet No. 65 C/N.W. The strike of the specimen is N.W.-S.E. dipping 80 degrees to the S.W. The specimen is fleshy red in colour and has a sub-vitreous lustre. It is very compact, hard and phaneric. It is mostly equigranular and fine-grained. Most of the grains are spherical in shape and a few are elongated. The rock is made up wholly of quartz.

Quartzite B.—This is taken from the same area as the above and the strike of the specimen is N.N.W.-S.S.E. and dips 35 degrees to the S.E. The megascopic and microscopic description is the same as above.

Marble A.—This is taken from Manditog north of Singareni Collieries (Hyderabad) included in the Survey of India Topo Sheet No. 65 C/N.W. The strike of the specimen is N.W.-S.E. and dips 15 degrees to S.W. The specimen is white in colour and shows a pearly lustre. It is very compact and phaneric. Most of the rock is made up of Calcite and Dolomite. It is rather fine-grained and equigranular. Most of the grains are elongated, exhibiting twinkling. A few accessories like Hornblende and Mica flakes are noticed.

Marble B.—This is also taken from the same locality as above and the strike of the specimen is N.E.-S.W. dipping 45 degrees to S.E. It is black in colour and the megascopic and microscopic characters are the same as above.

Granite A.—The granite is taken from the Osmania University area in the outskirts of Hyderabad City. The specimen is having a strike of N.W.-S.E. and slopes S.W. with an amount of 85 degrees. It has characteristic pink colour. It is very hard and compact with a pitted surface. It is medium to coarse grained. Quartz, Feldspar and other accessories are present in the specimen.

Granite B.—This is also taken from the same locality as above but the strike of the specimen is N.W.-S.E. with a slope of 55 degrees in S.E. The megascopic and the microscopic description of the rock is essentially the same but for small differences.

3. EXPERIMENTAL RESULTS

Sections of 0·5 to 1·0 inch square of the specimens described above are cut perpendicular to three specific geological directions and the ultrasonic velocities in these sections have been determined by the Wedge method

(Bhagavantam and Bhimasenachar, 1944). Two specimens of each rock are chosen in the present investigation and the results given in the following table.

TABLE I

No.	Rock	Direction	Thickness in mm.	Fundamental in m.c.s.	Velocity in m./sec.
1	Granite A ..	⊥ to Strike	1·90	1·60	6080
		to Dip	2·17	1·33	5772
		to both	2·17	1·45	6293
2	Granite B ..	⊥ to Strike	2·15	1·40	6020
		to Dip	2·15	1·45	6235
		to both	2·20	1·42	6248
3	Quartzite A ..	⊥ to Strike	2·04	1·38	5630
		to Dip	2·03	1·43	5684
		to both	1·98	1·40	5544
4	Quartzite B ..	⊥ to Strike	2·02	1·25	5050
		to Dip	2·04	1·24	5059
		to both	2·01	1·24	4984
5	Marble A ..	⊥ to Strike	1·96	1·93	7565
		to Dip	1·94	1·92	7450
		to both	2·02	1·94	7696
6	Marble B ..	⊥ to Strike	1·95	1·60	6240
		to Dip	1·94	1·61	6246
		to both	1·93	1·62	6253

Model composition of each of the sections studied for Granite A and the grain size variation in them are given in Table II.

TABLE II

Model Composition and Grain Size of Granite A

Mineral	⊥ to Strike %	⊥ to Dip %	⊥ to both %
Quartz	27·5	34·1	32·5
Felspar	63·8	59·7	58·1
Mafics	8·7	6·2	9·4
Grain size (mm.) ..	0·62–2·68	0·75–5·10	0·50–4·50

4. DISCUSSION OF RESULTS

The experimental results of percentage anisotropy observed in different rocks by different workers are given in Table III. It must be remarked here that the values given are for rocks of different geological formations worked under different conditions by different methods.

TABLE III

Rock	Zisman %	Ide %	Birch and Bancroft %	Prasada-rao %	Author %
Marble	25	30	..	33	3
Gneiss	50	3	5	31	..
Limestone	50	P. 2 S. 30	..	41	..
Trap	1	2	..	25	..
Granite	1	10 to 20	1	28	5 to 8
Quartzite	20	20	3	..	3

The results given in Table III, can be divided into two broad groups. Zisman and Prasadarao showed that there is marked anisotropy in rocks like Marble, Gneiss and Limestone. Zisman's results, however, indicate perfect isotropy in the case of Vinal haven trap and Quincy granite. On the contrary, the results of Ide, Birch and Bancroft show that there is no anisotropy of such a marked degree. The author's results are in good agreement with those of the latter observers. As is evident from Table III, Ide's results show that there is anisotropy to the extent of 10 to 30% in the case of Granite, Quartzite, Marble and Limestone (P). His results in the case of (S) limestone, Gneiss and Vinal haven trap show that the anisotropy is of the order of 2 to 3%. Such a difference in the percentage anisotropy between S limestone and P limestone is interesting. In the case of Gneiss the static value of Zisman shows an anisotropy of more than 50% while the dynamic values of Ide and Birch and Bancroft show very little departures from perfect isotropy in the case of Quartzite, Granite and Gneiss. Perfect isotropy in quartzite has also been observed by Sundararao. The results obtained in the present investigation in the case of Granite, Quartzite and Marble show that the percentage anisotropy is of the order of 1 to 8% only. Moreover, Zisman, Ide, Birch and Bancroft used specimens in the form of

right circular cylinders, usually about 20 cm. long and 2 cm. or less in diameter and it appears that in the case of certain rocks, departures from isotropy may be due to large-scale mineralogical and structural variations existing in such big specimens. Contrary to this, the specimens used by the present author are of such small dimensions that no such variations can be expected. Thus, it is clear that the percentage anisotropy in the case of rocks varies from specimen to specimen and is also influenced to some extent by the size of the specimen and according as the method employed is a dynamic or a static one.

The percentage anisotropy in the case of quartzites and marbles, as observed by the author, is only of the order of 1 to 3%. This is not much larger than possible experimental errors and is in agreement with the fact that these rocks are monomineralic and equigranular in nature as has been pointed out earlier. On the other hand, Granite, which is characterised by its variation in mineral composition and inequigranularity shows an anisotropy of 5 to 8%. This fact is corroborated by the results obtained by the author in a study of the model composition of these three granite sections, using a Dollar's stage and given in Table II. In the same table, the grain size variations of quartz in the three sections are also shown.

Summary

The directional variation of ultrasonic velocity has been studied in some of the Indian rocks. Quartzites and Marbles which are monomineralic show almost perfect isotropy. Granite shows a slight departure from isotropy (5 to 8%) which is attributed to the variation in mineralogical composition and in grain size from direction to direction.

In conclusion, the author desires to express his grateful thanks to Professor C. Mahadevan for his kind interest and guidance.

References

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2. Birch and Bancroft .. *Jour. Geol.*, 1938, **36**, 59.
3. Bridgman .. *The Physics of High Pressures*, 1931.
4. Ide .. *Rev. Sci. Inst.*, 1935, **6**, 296.
5. Prasadarao .. *Proc. Ind. Acad. Sci.*, 1947, **25A**, 238.
6. Sundararao .. *Ibid.*, 1948, **28A**, 185.
7. Zisman .. *Proc. Nat. Acad. Sci.* (*U.S.A.*), 1933, **19**, 666.

RANEY NICKEL REDUCTIONS

Part IV. Thioindigo Dyes, Thionaphthenes and Thiafluorenes

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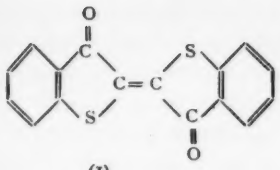
Desulphurization of thioindigo (Durindone Red B), 6:6′-diethoxythioindigo (Durindone Orange R) and thioindoxyl by the action of Raney alloy in aqueous alkali was discussed in Part II.[1] This method is useful for the determination of the constitution of sulphur-containing dyes and other organic compounds, and for the preparation of some of the products, such as the diphenacyl and 1:4-diphenylbutane derivatives, which are difficult to prepare by known methods. The latter may be expected to be formed by the desulphurization of the thioindigoid dyes, followed by reduction of the resulting sulphur-free compounds.

Degradation of thioindigoid dyes by treatment with alcoholic caustic potash,[2] ozonization,[3] and oxidation with fuming nitric acid,[4] involves the fission of the carbon chain linking the two aryl residues. Desulphurization of thioindigoid dyes by means of Raney nickel has the distinctive feature that the carbon skeleton of the molecule remains largely intact. Thus desulphurization of thioindigo (I) and 6:6′-diethoxythioindigo (II) by Raney alloy in aqueous alkali gave diphenacyl and 4:4′-diethoxydiphenacyl as the major products, although small amounts of benzoic acid, *p*-ethoxybenzoic acid and other by-products, were also obtained. Thioindigo gave 1:4-diphenylbutane when excess of Raney alloy was used. The present paper deals with the desulphurization of (I) and (II) under modified conditions, of other thioindigoid dyes, and of heterocyclic compounds containing sulphur as a part of the ring system.

Desulphurization of thioindigoid dyes with Raney alloy in aqueous alkali gave several reduction products, but treatment with Raney nickel in alcohol gave 1:4-diphenylbutanes, which were formed in good yields and were the only products isolated. Thus thioindigo gave 1:4-diphenylbutane (III) (yield 76%) and 6:6′-diethoxythioindigo gave 1:4-bis-*p*-ethoxyphenylbutane (IV) (yield 59%). The constitution of (III) and (IV) was proved by oxidation to benzoic acid and *p*-ethoxybenzoic acid.



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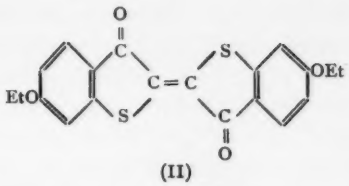

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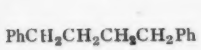

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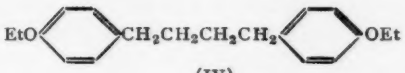
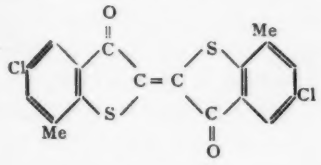
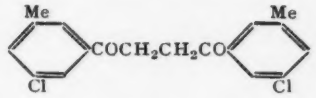


(IV)

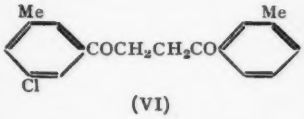
Treatment of 5: 5′-dichloro-7: 7′-dimethylthioindigo (Durindone Red 3BS) by Raney alloy in aqueous alkali left the dye largely unaffected, and it was found necessary to vat the dye before treatment with Raney alloy. When the dye, obtained in finely divided form by precipitation from sulphuric acid, was vatted with glucose and aqueous caustic soda and then treated with Raney alloy, the isolable sulphur-free degradation products were 3: 3′-dichloro-5: 5′-dimethyldiphenacyl (V), 5-chloro-3: 3′-dimethyldiphenacyl (VI) and 1: 4-di-*m*-tolyl-l-butanol (VII). When the dye was vatted by sodium hydrosulphite and aqueous alkali and then desulphurized by Raney alloy, a larger yield of the desulphurized product was obtained from which (V) and (VI) were again isolated, but the major constituent was a chlorine-free liquid which was not identified. Desulphurization of the dye by Raney nickel in boiling alcohol gave 1: 4-di-*m*-tolylbutane (VIII), the constitution of which was confirmed by oxidation to isophthalic acid. Cyclization of the diphenacyl derivative (V) gave 2: 5-di-(3′-chloro-5′-methyl)phenylfuran (IX).



Durindone Red 3BS



(V)



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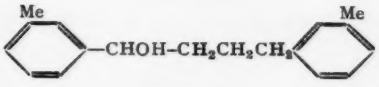
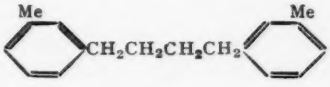


(VII)



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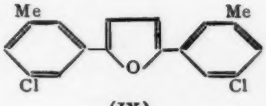
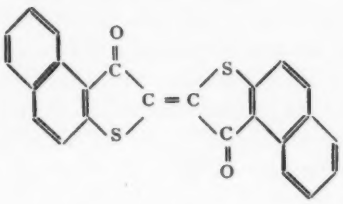
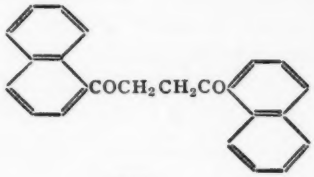


(IX)

Reduction of Durindone Brown GS (X), the naphthalene analogue of thioindigo, with Raney alloy in aqueous alkali gave 1:2-di-α-naphthoylethane (XI) and a yellow non-fluorescent liquid (b.p. 140–2°/12 mm.) which analysed for 1:4-di-α-tetralylbutane (XII). Cyclization of (XI) gave 2:5-di-α-naphthylfuran (XIII). When the dye was desulphurized with Raney nickel in alcohol a colourless liquid (b.p. 215–20°/1 mm.), exhibiting a blue fluorescence, was obtained, and it analysed for 1:4-di-α-tetralylbutane (XII). The two di-α-tetralylbutanes are apparently the 1:2:3:4- and 5:6:7:8-tetrahydronaphthalene derivatives.



(X)



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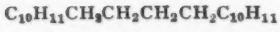

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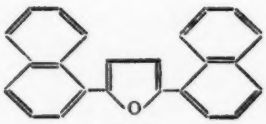
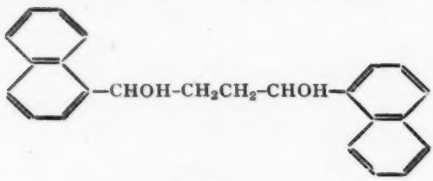


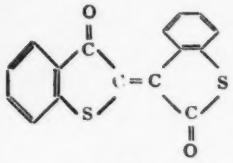
(XIII)

Ciba Brown 2R has been mentioned by Fox[5] as equivalent to Indanthrene Printing Brown 3R which is 2-(4:5-benzothionaphthene)-3′-(6′-chloro-7′-methylindole)-indigo; but elementary analysis of purified Ciba Brown 2R and the shade on cotton indicate that it is probably identical with Durindone Brown GS (X). This was confirmed by desulphurization with Raney alloy in aqueous alkali and with Raney nickel in alcohol, when Ciba Brown 2R gave the same reduction products as Durindone Brown GS. In one experiment Raney alloy alkali reduction of Ciba Brown GS also gave a small amount of a substance which was probably the diol (XIV).



(XIV)

The desulphurization of unsymmetrical dyes was next studied. On treatment with Raney alloy in aqueous alkali 2: 3′-bis-thionaphthene-indigo (XV) gave a compound which is probably constituted as 2: 4–diphenyl-1-butanol (XVI). The alternative structure 1: 3-diphenyl-1-butanol is improbable because Papa *et al.*[6] have shown that, under the conditions employed, a carbonyl group attached to a benzene nucleus is reduced to CH_2, whereas a carbonyl group not directly attached to the aryl residue undergoes reduction to an alcoholic group. Desulphurization of (XV) with Raney nickel in alcohol gave 1: 3-diphenylbutane (XVII).



(XV)

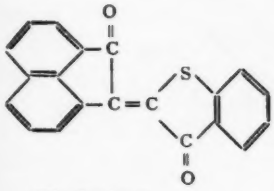
$PhCH_2CH_2\underset{Ph}{C}HCH_2OH$

(XVI)

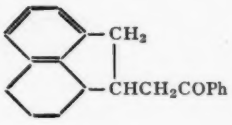
$PhCH_2CH_2\underset{Ph}{C}HCH_3$

(XVII)

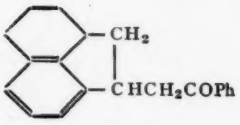
Desulphurization of Ciba Scarlet G by treatment with Raney alloy in aqueous alkali gave a complex mixture from which was isolated a pale yellow liquid, which analysed for $C_{20}H_{20}O$ and which probably has the structure (XVIII A) or (XVIII B). Desulphurization of the dye by Raney nickel in alcohol gave a hydrocarbon, $C_{20}H_{28}$, which may be represented as α-perhydro-acenaphthenyl-β-phenylethane (XIX). Attempts to dehydrogenate (XIX) by treatment with selenium were unsuccessful.



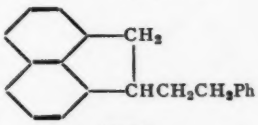
Ciba Scarlet G



(XVIII A)



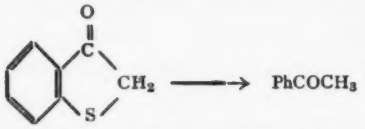
(XVIII B)



(XIX)

Blicke and Sheets[7] obtained ethylbenzene by the action of Raney nickel on thionaphthene, thioindoxyl, acetophenone or methyl phenyl carbinol in boiling alcoholic solution. By treatment of thioindoxyl with Raney nickel

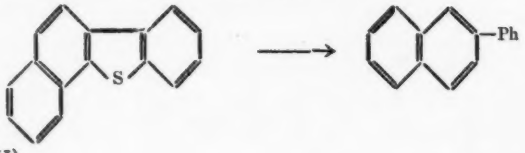
in aqueous sodium hydroxide at 0–5° we have obtained acetophenone in 72% yield. Desulphurization of 3-hydroxythionaphthene-2-carboxylic acid



(thioindoxylic acid, XX) was next studied under various conditions. Under mild conditions benzoylacetic acid was probably formed as the first step in the desulphurization but the major product isolated was always β-phenyl-β-hydroxypropionic acid. β-Phenylpropionic acid and acetophenone in the form of the 2 : 4-dinitrophenylhydrazone were also isolable. Thioindoxylic acid was completely desulphurized in 5 minutes by the action of Raney nickel in ice-cold aqueous alkali with the formation of β-phenyl-β-hydroxypropionic acid as the main product.

XX)

The constitution of 1 : 2-benzo-9-thiafluorene (XXI) and 3 : 4-benzo-9-thiafluorene (XXII), which have been recently reported,[8] was proved by desulphurization with Raney nickel in alcohol. The former gave 2-phenylnaphthalene and the latter 1-phenylnaphthalene.



(XXI)

(XXII)

EXPERIMENTAL

Reduction of thioindigo (I)

Thioindigo (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered. The filtrate, on removal

of alcohol, gave a liquid which was dissolved in ether and extracted with 5% sodium bicarbonate solution. Removal of ether gave a liquid (2·7 g.) which on distillation (b.p. 140–50°/2 mm.) gave a pink solid, m.p. 45–47° undepressed when mixed with 1 : 4-diphenylbutane (III), obtained in a previous degradation of the dye (*see* Part II).[1]

Oxidation of (III)

A mixture of (III) (0·2 g.) and 5% nitric acid (22·5 c.c.) was heated in a sealed tube at 150–80° for 12 hours. The mixture was extracted with ether. The ether extract was shaken with 5% sodium bicarbonate solution. The bicarbonate extract was acidified and ether extracted. Removal of ether gave a cream coloured product (0·2 g.) which was crystallized from water. A pale yellow solid (0·025 g., m.p. 170–75°), which contained nitrogen, first separated and was filtered off. The mother liquor was concentrated when needles (0·1 g.), m.p. 117–18°, were obtained. Recrystallization from water gave colourless needles, m.p. 122°, undepressed when mixed with benzoic acid.

Reduction of Durindone Orange R (II)

Durindone Orange R (12 g.) was extracted with boiling water and the residue (5 g.) was reduced with Raney nickel (50 g.) in boiling alcohol (500 c.c.) for 7 hours under stirring. The mixture was left overnight and filtered. The filtrate on removal of alcohol gave a sticky product (A) (0·93 g.). The nickel residue was treated with hydrochloric acid, filtered, washed and extracted in a Soxhlet with acetone and benzene. The residue obtained on removal of the solvents was extracted with ether. Removal of ether gave a low melting product (2·4 g.). The mixture of the latter with (A) was distilled at 145–50°/2 mm. and crystallized from alcohol in colourless plates, m.p. 74–76°, raised to 76–77° by recrystallization from the same solvent. It analysed for 1 : 4-bis-*p*-ethoxyphenylbutane (IV) (Found: C, 81·0; H, 8·6. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·7%).

Oxidation of (IV)

A mixture of (IV) (0·45 g.) and 5% nitric acid (32 c.c.) was heated in a sealed tube at 150–80° for 12 hours. The crude acid, isolated by extraction with aqueous sodium bicarbonate, crystallized from aqueous alcohol in colourless needles, m.p. 195°, undepressed when mixed with *p*-ethoxybenzoic acid.

Reduction of Durindone Red 3BS

Method A.—Durindone Red 3BS was purified by successive extractions with boiling water and 5% boiling hydrochloric acid. The purified dye

(10 g.) was precipitated from a solution in oleum, filtered and washed. The wet cake was vatted with glucose (50 g.) and 10% caustic soda solution (500 c.c.) at 70–80°. The solution was treated with Raney alloy (95 g.) in 10% caustic soda solution (500 c.c.) for 7 hours on a water-bath, left overnight, and filtered. The nickel residue was treated with hydrochloric acid, filtered, washed and extracted with benzene in a Soxhlet. The product (3·6 g.) recovered from the extract, was ether-extracted when an insoluble residue (0·35 g.) was obtained which crystallized from aqueous acetone in colourless plates, m.p. 180–81°. It analysed for 3:3′-dichloro-5:5′-dimethyldiphenacyl (V) (Found: C, 64·6; H, 5·2. $C_{18}H_{16}Cl_2O_2$ requires C, 64·5; H, 4·8%). The ether extract, after removal of the above product, gave an oil (3·2 g.) which was treated with *n*-hexane. A brown product (0·51 g.) separated which crystallized from aqueous acetone in colourless plates, m.p. 113–14°. It analysed for 5-chloro-3:3′-dimethyldiphenacyl (VI) (Found: C, 71·3; H, 6·4. $C_{18}H_{17}ClO_2$ requires C, 71·9; H, 5·6%). The product (2·64 g.), obtained from the hexane solution, was distilled when a pale yellow liquid, b.p. 196–200°/10 mm. was obtained. It analysed for 1:4-bis-*m*-tolyl-1-butanol (VII) (Found: C, 84·4; H, 8·3. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%). Attempts to isolate pure degradation products from the alkaline solution obtained after removal of nickel were unsuccessful.

Method B.—The commercial dye (6 g., containing 4·5 g. of the pure dye) was vatted with sodium hydrosulphite (6 g.) and 1·5% caustic soda solution (1,000 c.c.) at 85°. Caustic soda (20 g.) was added, followed by Raney alloy (50 g.). The mixture was stirred for 2 hours on a water-bath and filtered. The filtrate, as in Method A, did not yield any pure products. The nickel residue was extracted with benzene as in Method A. The sticky product (2·0 g.), obtained on removal of benzene, was extracted with ether. The ether-insoluble product (0·3 g.) crystallized from alcohol in colourless plates, m.p. 176–78°, undepressed when mixed with (V). The product from the ether solution was treated with *n*-hexane. The hexane-insoluble solid (0·33 g.) was dissolved in benzene and chromatographed on alumina. The major fraction gave colourless plates, m.p. 112–13°, from aqueous acetone, undepressed when mixed with (VI). The hexane-soluble liquid (1·3 g.) on distillation gave a chlorine-free liquid, b.p. 165–70° (Found: C, 83·5; H, 8·1%).

Method C.—The purified dye (5 g.) was reduced with Raney nickel (50 g.) in boiling alcohol (500 c.c.) for 7 hours under stirring and filtered hot. The product obtained from the alcoholic solution was dissolved in ether and extracted with aqueous sodium bicarbonate. Removal of ether gave an oil (2 g.) which was dissolved in benzene, and chromatographed on

alumina. The major zone yielded a product (1·8 g.), which on distillation gave 1:4-di-*m*-tolylbutane (VIII), colourless liquid, b.p. 145–50°/1·5 mm. (Found: C, 90·6; H, 9·4. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%).

Oxidation of (VIII)

A mixture of (VIII) (0·10 g.) and 5% nitric acid (22·5 c.c.) was heated in a sealed tube at 150–80° for 12 hours. The pale yellow product (0·026 g.) crystallized from water in colourless needles, m.p. 332–33°, undepressed when mixed with isophthalic acid.

2:5-*Di*-(3′-*chloro*-5′-*methyl*) *phenylfuran* (*IX*)

A mixture of (V) (0·1 g.), glacial acetic acid (5 c.c.) and concentrated hydrochloric acid (5 c.c.) was refluxed for 3 hours and poured over crushed ice. The product which separated was filtered and washed. Crystallization from alcohol gave colourless needles, m.p. 162–63°, of the furan (IX) (Found: C, 67·7; H, 4·7. $C_{18}H_{14}Cl_2O$ requires C, 68·1; H, 4·4%).

Reduction of Durindone Brown GS

Method A.—Durindone Brown GS was extracted with boiling water and boiling 5% hydrochloric acid, filtered, washed and dried. The purified dye (20 g.) was precipitated from concentrated sulphuric acid and the wet cake was treated with Raney alloy (90 g.) in 10% caustic soda solution (900 c.c.) on a water-bath for 1½ hours. The mixture was filtered. The alkaline filtrate did not yield any organic material. The nickel residue was extracted with benzene, and evaporation of the solvent gave a dark coloured product (14·12 g.), which was extracted with ether. The ether-insoluble solid (5·61 g.) crystallized from alcohol in colourless plates, m.p. 141–42°, undepressed when mixed with 1:2-di-α-naphthoylethane (XI), prepared according to Lutz *et al.*[9] The ether extract after separation of the above product gave an oil (8·51 g.), which was distilled. The fraction boiling at 140–42°/12 mm. was a yellow liquid which analysed for 1:4-di-α-tetralylbutane (XII) (Found: C, 90·3; H, 9·3. $C_{24}H_{30}$ requires C, 90·6; H, 9·4%).

Method B.—The purified dye (5 g.) was treated with Raney nickel in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. Removal of alcohol gave an oil (2·0 g.), which was dissolved in benzene and chromatographed on alumina. The major zone gave a product (1·9 g.), which distilled as a colourless liquid, b.p. 215–20°/1 mm., having a blue fluorescence in ultraviolet light and analysing for 1:4-di-α-tetralylbutane (XII) (Found; C, 90·0; H, 9·0. $C_{24}H_{30}$ requires C, 90·6; H, 9·4%).

2:5-Di-α-naphthylfuran (XIII)

A mixture of (XI) (0·2 g.), glacial acetic acid (5 c.c.) and concentrated hydrochloric acid (8 c.c.) was refluxed for 6½ hours and added to crushed ice. Crystallization of the product from alcohol gave colourless plates, m.p. 85–86°, which analysed for the furan (XIII) (Found: C, 89·4; H, 5·0. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%).

Reduction of Ciba Brown 2R

Ciba Brown 2R was purified by successive extractions with boiling water and with 5% boiling hydrochloric acid, filtered, washed and dried. Three crystallizations from *o*-dichlorobenzene gave brown needles, which did not contain chlorine or nitrogen (Found: S, 16·1. Calc. for $C_{24}H_{12}O_2S_2$: S, 16·2%).

Method A.—The purified dye (5 g.) was precipitated from concentrated sulphuric acid and the wet cake was treated with Raney alloy (27·5 g.) in 10% caustic soda solution (275 c.c.) for 5 hours on a water-bath. The mixture was filtered and the nickel residue extracted with benzene as usual. On cooling the benzene extract (300 c.c.), a substance (0·1 g.) separated which crystallised from benzene in colourless plates, m.p. 213–14° (Found: C, 83·5; H, 6·7. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·2%). The stated theoretical figures for C and H are for 1:4-di-α-naphthyl-1:4-butanediol (XIV). The benzene mother liquor was concentrated to 20 c.c. and cooled, when a colourless substance (0·61 g.) separated, which crystallized from alcohol in colourless plates, m.p. 139–40°, undepressed when mixed with (XI). The benzene mother liquor on removal of the solvent gave an oil (2·3 g.), which after repeated distillation, gave a colourless liquid, b.p. 225°/7–8 mm., showing a blue fluorescence in ultraviolet light (Found: C, 90·2; H, 9·0. $C_{20}H_{30}$ requires C, 90·6; H, 9·4%). The required C, H values are for 1:4-di-α-tetralylbutane (XII).

Method B.—The purified dye (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. The filtrate on removal of alcohol gave an oil (1·84 g.), which was dissolved in benzene and chromatographed on a column of alumina. The major zone gave a product (1·7 g.) which distilled as a colourless liquid, b.p. 220–25°/1 mm., exhibiting a blue fluorescence in ultraviolet light, and analysing for 1:4-di-α-tetralylbutane (XII) (Found: C, 90·1; H, 9·2. $C_{24}H_{30}$ requires C, 90·6; H, 9·4%).

Reduction of 2:3′-bis-thionaphthene-indigo (XV)

Method A.—2:3′-Bis-thionaphthene-indigo (5 g.) was treated with Raney alloy (22·5 g.) in 10% caustic soda solution (225 c.c.) for 2 hours on a water-

bath and the mixture filtered. The nickel residue was extracted with benzene as usual, and the oil (1·0 g.) obtained was dissolved in benzene and chromatographed on a column of alumina. The major zone led to a yellow liquid (0·4 g.), b.p. 165–70°/7 mm., having a bluish violet fluorescence and analysing for 2: 4-diphenyl-1-butanol (XVI) (Found: C, 85·2; H, 8·4. $C_{16}H_{18}O$ requires C, 85·0; H, 8·0%).

Method B.—2: 3′-Bis-thionaphthene-indigo (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. The filtrate, on removal of alcohol, gave a red, bicarbonate-insoluble liquid (2·7 g.) which was dissolved in benzene and chromatographed on alumina. The major zone gave a colourless liquid (1·7 g.), b.p. 105–10°/1 mm., which analysed for 1: 3-diphenylbutane (XVII), prepared earlier by Stobbe and Posnjak[10] (Found: C, 91·3; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%).

Reduction of Ciba Scarlet G

Ciba Scarlet G was purified by successive extraction with boiling water and boiling 5% hydrochloric acid. The purified dye crystallized from benzene in scarlet needles, m.p. 269–70° (Found: S, 9·9. Calc. for $C_{20}H_{10}O_2S$: S, 10·2%).

Method A.—The purified dye (10 g.) was precipitated from concentrated sulphuric acid and the wet cake was treated with Raney alloy (45 g.) in 10% aqueous caustic soda solution (450 c.c.) for 90 minutes on a water-bath and filtered. The nickel residue was treated as usual and extracted with alcohol. The product (8·86 g.) obtained from the alcoholic extract was dissolved in carbon tetrachloride and chromatographed on alumina, when it separated into 6 zones. The major zone yielded a thick brown liquid which was re-chromatographed, when it again separated into 5 zones. The major zone gave a pale yellow liquid, b.p. 170–75°/5 mm. which analysed for (XVIII) (Found: C, 87·5; H, 7·2. $C_{20}H_{20}O$ requires C, 87·0; H, 7·2%). It gave a 2: 4-dinitrophenylhydrazone which could not however be crystallised.

Method B.—The purified dye (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. The product (2·9 g.) obtained on removal of alcohol was dissolved in benzene and chromatographed on alumina. The major zone gave a yellow oil (2·7 g.), b.p. 168–72°/1 mm., analysing for (XIX) (Found: C, 89·3; H, 9·4. $C_{20}H_{28}$ requires C, 89·6; H, 10·4%).

Reduction of thioindoxyl

" Thioindoxyl melt " (I.C.I., 40 g.) was dissolved in cold water (200 c.c.), the solution treated with norit and filtered. The filtrate was cooled and acidified by cold dilute sulphuric acid. The precipitate of 3-hydroxythionaphthene-2-carboxylic acid (XX) was suspended in water and made alkaline to Brilliant Yellow paper by addition of 5% caustic soda solution. The solution was stirred on a water-bath at 60–70° to effect decarboxylation of thioindoxylic acid (XX). After the decarboxylation was complete (30 minutes) the mixture was made alkaline (phenolphthalein), treated with norit and filtered. The alkaline solution was cooled and acidified. The very pale pink precipitate of thioindoxyl was washed with cold water and dried in a vacuum. The substance (7·7 g.) was treated with Raney nickel (50 g.) in 10% caustic soda solution (250 c.c.) at 0–5° for 90 minutes and filtered. The alkaline filtrate was extracted with ether. The ether extract on removal of the solvent gave an oil (4·43 g.). Fractionation yielded a colourless liquid, b.p. 202–3°. It formed a 2 : 4-dinitrophenylhydrazone, m.p. 236–37° (*dec.*) undepressed when mixed with acetophenone dinitrophenylhydrazone.

Reduction of thioindoxylic acid (XX)

Method A.—Thioindoxylic acid (5 g.), prepared as above from thioindoxyl melt (20 g.), was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 9 hours and filtered hot. The alcoholic filtrate, on removal of solvent, gave a liquid (1·6 g.) which was extracted with 10% sodium bicarbonate solution. The bicarbonate-insoluble liquid (0·34 g.) distilled at 100–40°, and it did not give a dinitrophenylhydrazone. The bicarbonate solution, on acidification and ether extraction, gave a liquid (1·2 g.). This was extracted with petroleum ether (b.p. 65–75°), when a solid (0·19 g.), m.p. 84–6°, separated, which crystallized from benzene in colourless prisms, m.p. 92°, undepressed when mixed with β-phenyl-β-hydroxypropionic acid. The petroleum ether solution on concentration and cooling gave colourless prisms, m.p. 46–7°, undepressed when mixed with β-phenylpropionic acid.

Method B.—Thioindoxylic acid (5 g.) was treated for 5 minutes with Raney nickel (50 g.) and 3% caustic soda solution (150 c.c.) in an ice-bath under stirring, and the mixture filtered. The filtrate on ether extraction did not yield any alkali-insoluble product. The alkaline solution was cooled and made slightly acidic with cold dilute hydrochloric acid, and ether extracted. The extract on removal of ether in a current of dry air gave an orange-coloured liquid. On trituration with petroleum ether a solid (2·0 g.)

separated, which crystallized from benzene in colourless prisms, m.p. 92°, undepressed when mixed with β-phenyl-β-hydroxypropionic acid. The petroleum ether solution, on removal of solvent, yielded a sticky substance (1·1 g.), which contained acetophenone identified as the 2:4-dinitrophenylhydrazone.

Reduction of 1 : 2-*benzo*-9-*thiafluorene* (*XXI*)

A mixture of (XXI) (0·8 g.), Raney nickel (8 g.) and alcohol (100 c.c.) was refluxed under stirring for 2½ hours and filtered hot. Removal of alcohol from the filtrate gave a sticky substance (0·68 g.). It was distilled at 130–50°/0·7 mm., when a colourless liquid distillate was obtained which soon solidified. Crystallization from alcohol gave colourless plates, m.p. 100–1°, undepressed when mixed with 2-phenylnaphthalene prepared according to Hey *et al.*[11]

Reduction of 3:4-*benzo*-9-*thiafluorene* (*XXII*)

A mixture of (XXII) (0·8 g.), Raney nickel (8 g.) and alcohol (100 c.c.) was refluxed under stirring for 3½ hours and filtered hot. The alcoholic filtrate on removal of solvent gave a red liquid (0·57 g.). The fluorescent solution in benzene was chromatographed on alumina in ultraviolet light. The major zone gave an orange liquid (0·47 g.), which distilled at 135–40°/1 mm. to a colourless liquid with a blue fluorescence (Found: C, 93·7; H, 6·4. Calc. for $C_{16}H_{12}$: C, 94·1; H, 5·9%). The absorption spectrum was identical with that of 1-phenylnaphthalene.[12]

Summary

Desulphurization of the following thioindigoid dyes has been studied: Durindone Red B, Durindone Orange R, Durindone Red 3BS, Durindone Brown GS, Ciba Brown 2R and Ciba Scarlet G. The action of Raney alloy in aqueous alkali gave diphenacyl derivatives in most cases together with further reduction products, such as 1:4-diaryl-1:4-butanediols and 1:4-diaryl-1-butanol. Reduction of the dyes with Raney nickel in alcohol gave 1:4-diarylbutanes as the major products. The chlorine atoms in Durindone Red 3BS were partially or completely removed during the reduction. The constitution of Ciba Brown 2R was proved by reduction and the dye was shown to be identical with Durindone Brown GS. The constitution of the diphenacyls was proved by conversion to 1:4-diarylfurans and by synthesis. The constitution of 1:4-diarylbutanes was proved by oxidation to the corresponding benzoic acids. Reduction of 2:3′-bis-thionaphthene-indigo gave an alcohol, probably constituted as 2:4-diphenyl-1-butanol.

Mild reduction of thioindoxyl gave acetophenone, thioindoxylic acid gave β-phenyl-β-hydroxypropionic acid, together with dihydrocinnamic acid.

The constitution assigned earlier to 1:2-benzo- and 3:4-benzo-9-thiafluorenes was confirmed by their desulphurization to β- and α-phenylnaphthalene respectively by means of Raney nickel.

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CHEMICAL EXAMINATION OF PLANT INSECTICIDES

Part VIII. Pods of *Tephrosia lanceolata* Grah.

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Preliminary trials with different parts of the plant *Tephrosia lanceolata* indicated that besides the roots (whose examination has been described in Parts VI and VII of this series[1, 2]) alcoholic extracts of the pods and flowers are also toxic to fish (pods: 134 p.p.m. in 50 minutes; flowers: 333 p.p.m. in 30 minutes). The results of a chemical study of the pods are described herein.

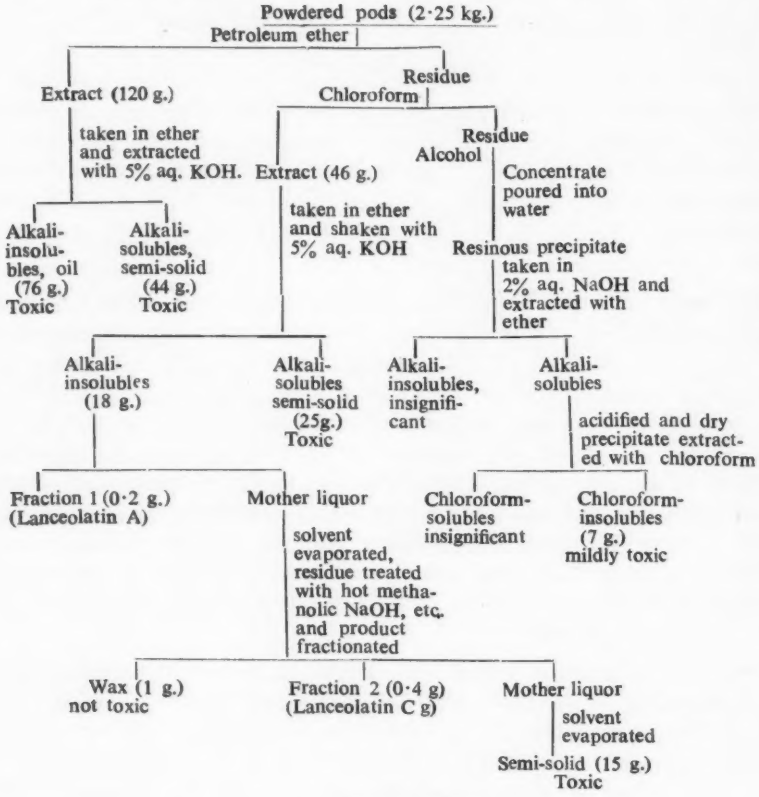
The pods were powdered and extracted successively with petroleum ether, chloroform and methylated spirit. No crystalline compound separated from the petroleum ether extract. Though pure rotenoids are almost insoluble in petroleum ether, the possibility of their dissolving in that solvent along with other amorphous substances is indicated by the work of Haller and LaForge[3] and Merz and Schmidt.[4] Hence in order to facilitate the separation of any crystalline components that might be present, the total petroleum ether extract was taken in ether and separated into alkali-soluble and alkali-insoluble portions by shaking with aq. potash. Though both fractions exhibited toxicity to fish (alkali-insolubles: 534 p.p.m. in 13 minutes; alkali-solubles: 150 p.p.m. in 3 hours), they did not yield crystalline components from any solvent.

The total chloroform extract was divided as usual into alkali-soluble and alkali-insoluble portions. The alkali-insoluble portion yielded only one crystalline component through direct crystallisation. This was found to be identical with Lanceolatin A (described under the name Substance I in Part VI[1]). The amorphous portion was subjected to treatment with boiling 1% methanolic sodium hydroxide (*cf.* Part VII[2]). The reaction product yielded crystalline Lanceolatin C (first described in Part VII), a non-toxic wax and a toxic semi-solid residue (49 p.p.m. in 12 minutes).

Crystalline Lanceolatin B which accompanies Lanceolatin A and C in the root-bark of *T. lanceolata* (see Parts VI and VII) could not be isolated from the pods.

The alkali-soluble part of the chloroform extract did not yield any crystalline component. It was toxic to fish (100 p.p.m. in 8 minutes).

The alcohol extract of the pods proved to be amorphous. It was soluble in alkali but insoluble in chloroform. Toxicity was feeble, 133 p.p.m. in 2½ hours. Boiling with aqueous or alcoholic KOH did not lead to the isolation of any crystalline substances.


Powdered pods (2·25 kg.)
Petroleum ether
Extract (120 g.)
Residue
Chloroform
taken in ether and extracted with 5% aq. KOH.
Residue
Alcohol
Extract (46 g.)
Concentrate poured into water
Alkali-insolubles, oil (76 g.) Toxic
Alkali-solubles, semi-solid (44 g.) Toxic
taken in ether and shaken with 5% aq. KOH
Resinous precipitate taken in 2% aq. NaOH and extracted with ether
Alkali-insolubles (18 g.)
Alkali-solubles semi-solid (25g.) Toxic
Alkali-insolubles, insignificant
Alkali-solubles
acidified and dry precipitate extracted with chloroform
Fraction 1 (0·2 g.) (Lanceolatin A)
Mother liquor
Chloroform-solubles insignificant
Chloroform-insolubles (7 g.) mildly toxic
solvent evaporated, residue treated with hot methanolic NaOH, etc. and product fractionated
Wax (1 g.) not toxic
Fraction 2 (0·4 g) (Lanceolatin C g)
Mother liquor
solvent evaporated
Semi-solid (15 g.) Toxic

EXPERIMENTAL

Only the working up of the chloroform extract is described here in detail. The solvent-free extract (46 g.) was taken up in ether (500 c.c.) and shaken with 5% aqueous potassium hydroxide (4 × 50 c.c.). The ether solution was washed neutral, dried, filtered, concentrated and left in the ice-chest for a week. The crystalline solid that separated was filtered off (Fraction 1). The amorphous residue (17 g.) recovered from the mother liquors was taken

into 80 c.c. of methanol, treated with 20 c.c. of 5% aqueous sodium hydroxide and refluxed for 30 minutes. The reaction product was diluted with water, acidified with hydrochloric acid (congo red paper) and extracted with chloroform (3 × 50 c.c.). The residue obtained on removing the chloroform was treated with methanol (100 c.c.) and warmed to 50°. The heterogeneous mixture was transferred to a separating funnel while still warm. The lower oily layer was drawn off; on cooling it solidified to the consistency of a wax (1 g.). The methanol solution was filtered, concentrated to low volume and left in the ice-chest. The solid that separated (Fraction 2) was filtered and washed with a few c.c. of methanol. The mother liquor and washings yielded a semi-solid residue (15 g.) on evaporation.

Fraction 1 (0·2 *g.*).—Crystallisation from methylated spirit and then from methanol-acetone yielded pale yellow needles melting at 186–88°. Colour reactions were identical with those of Lanceolatin A and the mixed m.p. was undepressed.

Fraction 2 (0·4 *g.*).—Crystallisation from ether, methanol-acetone and finally from ethyl acetate yielded pale orange thick hexagonal plates melting at 128–29°. Colour reactions were the same as those of Lanceolatin C and the mixed m.p. was undepressed.

Summary

The pods of *Tephrosia lanceolata* have been subjected to chemical study. The isolation of Lanceolatin A and Lanceolatin C (crystalline substances) in a very small yield and of a number of amorphous fractions, most of them toxic to fish, is described.

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